Development of a sustainable process to reduce CO_2 emissions using anaerobic treatment of industrial pulp and paper wastewater

Najmeh Abedi

A Thesis
In the Department
of
Building, Civil, and Environmental Engineering

Presented in Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy (Environmental Engineering) at
Concordia University
Montreal, Quebec, Canada

Nov. 2015

CONCORDIA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

This is to certify that the thesis prepared

By: Najmeh Abedi

Entitled: Development of a sustainable process to reduce CO2 emissions using anaerobic treatment of industrial pulp and paper wastewater

and submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy (Environmental Engineering)

complies with the regulations of this University and meets the accepted standards with respect to originality and quality.

Signed by the final examining commitee:

Dr. R. Ganesan,	Chair
Dr. Paul Stuart,	External Examiner
Dr. Justin powlowski,	Examiner
Dr. Fariborz Haghighat,	Examiner
Dr. Zhi Chen,	Examiner
Dr. Catherine Mulligan,	Co-Supervisor
Dr. Laleh Yerushalmi,	Co-Supervisor

Approved by _____

Chair of Department or Graduate Program Director

_____2015 _____

Dean of Faculty

Abstract

Atmospheric concentration of carbon dioxide (CO_2), a major component of greenhouse gases, has increased significantly since the beginning of the industrial revolution. Many attempts have been aimed at capturing, sequestering, and reducing carbon dioxide emissions, but they have not been very efficient and economical.

The objective of this work is to develop a sustainable system to reduce the carbon dioxide emissions by applying anaerobic treatment of wastewater. In this method, industrial emissions containing CO_2 are injected into a wastewater stream entering the anaerobic reactor where CO_2 is biologically converted to methane as a biogas. This conversion is based on the final step of anaerobic degradation in which methanogenic bacteria produce methane from acetic acid or CO_2 and hydrogen. Consequently, with the addition of carbon dioxide after wastewater pollutant degradation (that provides acetic acid and hydrogen), methane with a high efficiency can be produced through a highly sustainable process.

To investigate the feasibility of this process for CO_2 removal, two series of batch tests using the Chemi-Thermomechanical Pulping (CTMP) and recycled pulp and paper wastewater were performed. In this project pulp and paper wastewater was selected since this industry produces a large amount of wastewater and is responsible for a large portion of CO_2 emissions. In order to determine the optimal conditions, the effect of different parameters such as pH (5.5 - 7.5), and temperature (30 - 35ºC) on the efficiency of CO_2 and COD removal and methane production was investigated.

As a conclusion of the first part of this work, it was shown that anaerobic treatment can be used to remove carbon dioxide by bioconversion to methane. By applying this method, CO_2 concentration will be reduced and methane will be produced simultaneously. The results show that at all pH values examined in the present work, CO_2 removal by bioconversion into methane is higher in samples with CO_2 injection compared to the control samples with no CO_2 injection. Results also showed that CO_2 removal was higher at lower pH values. For example, for CTMP wastewater at pH 7.5 and 35°C the CO_2 removal by bioconversion into methane in samples with CO_2 injection was 13 mg/l (19%) higher than the control sample, while this value at pH 5.5 was

515 mg/l (29%) higher than the control sample. At 35°C and at all pH values, the increase in CO_2 removal by bioconversion to methane in samples with CO_2 injection compared to the control samples with no CO_2 injection was 3-6% higher than that obtained at 30°C. The best efficiency for CO_2 removal occurred at pH 5.5 and 35ºC.

Operating pH and temperature and injection of CO_2 didn't show significant impact on COD removal, although higher COD reduction rates were achieved at higher temperature. It was shown that COD reduction rates were almost similar at different pH values. Temperature has a significant impact on methane generation at all operating pH. Injection of carbon dioxide had a positive impact on methane production and in samples with CO_2 injection more methane generation was observed.

Although at higher pH values methane generation is higher than that at lower pH values, the increase in methane generation by the injection of CO_2 to the wastewater is lower. The reason for this observation is that at a higher pH of 7 and 7.5, only a small amount of CO_2 was dissolved in the wastewater and was later converted to methane. Therefore, at higher pH values, the difference in methane generation in the presence and absence of CO_2 injection was less than that observed at lower pH values.

In CTMP wastewater at 35ºC, the injection of CO_2 into the wastewater increased methane generation by 162 ml (108%) at pH 5.5 and by 22 ml (3%) at pH 7.5. For the recycled paper experiment at 35ºC, the injection of CO_2 into the wastewater increased methane generation by 54 ml (93%) at pH 5.5 and by 8 ml (4%) at pH 7.5.

The continuous experiments were performed following the batch tests in the UASB reactors at three organic loading rates (OLR of 1, 2, and 3g COD/l.d.) using CTMP wastewater for 115 days. Results showed that regardless of CO_2 injection and initial pH of wastewater, COD removal was almost equal from the reactor with CO_2 injection in the feed (R_2) and control reactors (R_1). The COD removal, equal to 70% was achieved at OLR=1 g COD/l.d, and its value gradually decreased to 65% at OLR=3g COD/l.d.

Methane generation in R_2 with CO_2 injection was higher than the control reactor with the same pH (pH 5.5) in its influent wastewater. However these values were less than the methane generation in the control reactor without pH adjustment (with influent wastewater of pH 6.5) that was more suitable for methanogenic activity. Methane generation in R_2 at OLR 1, 2 and 3 was approximately equal to 400-570, 960-1120, and 700-1700 ml/d, respectively, while these values

for R_1 reactor with pH adjustment were approximately equal to 200-300, 460-700, and 370-920 ml/d. The higher methane generation in R_2 compared to R_1 with pH adjustment is attributed to the bioconversion of CO_2 to methane. Results showed that approximately 83-97% of the injected dissolved CO_2 in R_2 was removed by the proposed pathways.

The potential GHG reduction and economic feasibility of the developed process was evaluated by applying detailed calculations. GoldSET^{TM} software was applied to compare the proposed developed process with conventional hybrid and aerobic treatment processes based on the sustainability aspects. The results of GoldSET software confirmed the higher sustainability of the developed hybrid treatment process compared to the conventional hybrid and aerobic treatment processes. Application of developed hybrid treatment process instead of conventional hybrid treatment process can annually save up to 3 million dollars in annual costs of treatment plants and will reduce GHG emissions by 100,000 tCO_2e/y.

A numerical method based on the Runge-Kutta fourth-order method was developed to investigate the controlling kinetic parameters for anaerobic digestion of carbon dioxide. Results showed that the values of kinetic parameters estimated from the two experimental setups were very close. The obtained values for K_s and μ_m for Cascades wastewater were 0.4g/l and 0.02/d, while these values for CTMP wastewater were 0.6 g/l and 0.025/d respectively. Results of both experiments showed that simulated values were in compliance with the experimental data and similar pattern during different experimental conditions were observed.

Acknowledgments

I would like to express my sincere gratitude to my supervisors, Dr. Catherine Mulligan and Dr. Laleh Yerushalmi for their constant support, encouragement and inspiring advices through the course of this thesis.

Additionally, I would like to appreciate all other supervisory committee members, Dr. Paul Stuart, Dr. Justin powlowski, Dr. Fariborz Haghighat, and Dr. Zhi Chen for accepting the appointment to the dissertation committee, as well as for their suggestions and support.

I acknowledge the FRQNT and Concordia University for their financial support and Golder Associates for providing the GoldSET software.

I would like to dedicate this thesis to my wonderful husband, Hosein, and my kind-hearted parents for all the supports and love they gave to me.

Table of Contents

List of Figures

List of Tables

Nomenclature

AC	Acetate ion
adt	Air dried ton
Alk	Alkalinity
Aq	Aqueous
Atm	Atmosphere
ATP	Adenosine Three Phosphate
CAS	Conventional Activated Sludge
CC	Carbon Credit
CCS	Carbon Capture and Sequestration
CH_3-S-CoM	Methyl-coenzyme M
CMP	Chemo-Mechanical Pulping
COD	Chemical Oxygen Demand
CO_2e	Equivalent Carbon Dioxide
CO_3^{2-}	Carbonate ion
CSTR	Continuous Stirred Tank Reactor
CT	Chemical Treatment
CTMP	Chemi-Thermomechanical Pulping
DMS	Dimethyl Sulphide
EGSB	Expanded Granular Sludge Bed Reactor
EOR	Enhanced Oil Recovery
Ex-AS	Extended Aeration Activated Sludge system
GC	Gas Chromatograph
GCEP	Global Climate and Energy Project
GHG	Greenhouse Gas
GLS	Gas, Liquid, Solid
GWP	Global Warming Potential
HCO_3^-	Bicarbonate ion
hp/1000 cfm	Horse power/1000 cubic feet per minute
HRT	Hydraulic Retention Time
IC	Internal Circulator reactor
IPCC	International Panel on Climate Change
k_d	Biomass decay rate
K_s	Half-saturation constant
kWh	kilo watt hour
LFG	Landfill Gas
MA	Methanogenic Activity
MITI	Ministry of International Trade and Industry

MM	Molar Mass
M$	Million dollar
N	Nitrogen
NCASI	National Council for Air and Stream Improvement
NOAA	National Ocean and Atmospheric Administration
NPV	Net Present Value
OLR	Organic Loading Rate
P	Phosphorus, Pressure
ppb	Parts per billion
R	Reactor
S	Substrate Concentration
scfm	Standard Cubic Feet per Minute
SEM	Scanning Electron Microscopy
SMA	Specific Methanogenic Activity
TCD	Thermal Conductivity Detector
tCO_2e	Ton CO_2 equivalent
TJ	Terra joule
TMP	Thermo-Mechanical Pulping
TSS	Total Suspended Solid
TWBG	The World Bank Group
UASB	Upflow Anaerobic Sludge Blanket
UNIDO	United Nations Industrial Development Organization
USEPA	United States Environmental Protection Agency
UV-VIS	Ultra Violet- Visible
VFA	Volatile Fatty Acid
Vol.	Volume
VSS	Volatile Suspended Solids
WW	Wastewater
WWS	Wind, Water power, and Solar
X	Microbial concentration in the bioreactor
Y	Microbial yield coefficient
μ	Growth rate of biomass
μ_m	Maximum growth rate of biomass

Chapter 1: Introduction

1.1 Problem Statement

1.1.1 Carbon dioxide: A dominant greenhouse gas (GHG)

Carbon dioxide is an important atmospheric gas that has a significant impact on the thermal radiation balance of the atmosphere, known as the "greenhouse" effect. This effect results in the increase of the average temperature of the earth surface which is called global warming (Niehaus, 1978). The global warming associated with carbon dioxide emissions has led to the decrease in the moisture level of soil and the onset of drought in some regions, large variations in regional climates, increase in evaporation and precipitations which can cause severe rain storms and hurricanes, and increase of the sea levels. These storms will become more intense and frequent as the increase of ocean temperatures increase evaporation.

An increase in the concentration of atmospheric CO_2 concentration also affects the carbon dioxide balance in the oceans and sea water. This affects the pH chemistry of sea water and will have an impact on aquatic organisms and ecosystems. Acidifying the ocean is particularly detrimental to organisms consisting of shell material of $CaCO_3$, such as coral reefs (Fabry et al., 2008).

Global warming became a serious issue after the industrial revolution in the eighteenth century in which human activities introduced a large amount of carbon dioxide, an important greenhouse gas (GHG), to the atmosphere. As a result, global and arctic average temperatures increased by more than 0.72°C, twice the increase during the previous century (Pachauri and Reisinger, 2007). The National Ocean and Atmospheric Administration (NOAA) reported an increase in the concentration of atmospheric carbon dioxide from 316 ppm in 1960 to 399.65 ppm in January 2015 (NOAA, 2015). Also, carbon dioxide accounts for 95% of directly emitted greenhouse

gases (GHGs); hence it is the main contributor to global warming (US EPA, 2012). The United States Environmental Protection Agency (US EPA) reported that slowing down the consumption of fossil fuels is the best method to reduce CO_2 emission. Power plants consume fossil fuels to generate electricity and they are among the major sources of CO_2 emission, accounting for 38% of the total U.S. CO_2 emissions in 2012 (US EPA, 2014). Nuclear energy is a prominent alternative for fossil fuels which can substantially reduce emissions of CO_2. However safety and security considerations, difficulty in construction and waste disposal are the obstacles that limit its application. Therefore, long term solutions for carbon dioxide reduction must be investigated that are environmentally safe, economically efficient, and socially acceptable.

Many attempts for carbon dioxide capture, sequestration and disposal have been made to decrease the CO_2 concentration in the atmosphere and oceans. In some processes, carbon dioxide is injected into underground waters, saline waters, aquifers, or deep oceans. In others, it is injected into deep surface rocks (geologic sequestration). However, the examined processes simply transfer CO_2 from the atmosphere to another location, and there is a risk of its rerelease to the atmosphere (Reeve, 2000; Herzog et al., 2003).

Applying CO_2 to neutralize alkaline wastewater is a method for its safe disposal (Gaur et al., 2009; Rao et al., 2007). Metallurgists consider carbon dioxide like other oxides and reduce it to its elements. This method needs extensive energy to overcome the positive free Gibbs energy of formation of CO_2 (Neelameggham, 2008). Permanent fixation of isolated CO_2 from the biosphere to insoluble minerals onto the sea bottom is another method (Katsuyoshi, 2008). Chemical and biological conversion of carbon dioxide to methane, a high-energy gas is also possible. Most of the methods that have been conventionally used for CO_2 reduction have limited applicability, low efficiency or high cost.

1.1.2 Wastewater from the pulp and paper industry

Rapid increase in human population and their vast demand for paper has led to a large growth in the paper industry. The pulp and paper production is a very water demanding industry that does not reuse its consumed water. A study by National Council for Air and Stream Improvement (NCASI) on the water profile of the U.S. forest products industry shows that approximately 88% of the consumed water is discharged to the surface waters following the treatment, and about 11% is converted to water vapor and emitted to the atmosphere (Flinders, 2009; Wiegand et al.

2011). The pulp and paper industry is the largest consumer of process water and is the third largest consumer of energy in the United States after the chemical and metal industries (U.S. Department of Commerce, 2000 and U.S. Department of Energy, 2000). It is the third largest consumer of energy in Canada after the mining and oil and gas extraction (Statistics Canada, 2010). Direct emissions associated with fuel combustion in the pulp and paper industry (excluding biomass CO_2) is equal to 57.7 million metric tonnes of CO_2e/y (US EPA, 2010). Pulp and paper industry has been shown to be a major consumer of natural resources which discharges a significant amount of pollutant to the environment (Thompson et al., 2001). In this industry, the pulping process is the main source of chemicals and toxic substances discharged to the environment. These chemicals and pollutants vary depending on the type of the applied pulping process. Discharging the effluent to surface waters without treatment introduces a large amount of toxic substances which endanger the lives of zooplankton and fish, as well as profoundly affecting the terrestrial ecosystem. They also lead to the formation of scum, thermal impact, slime growth, change in water color, and loss of aesthetic beauty in the environment.

Considering the vast pollution that can be caused by the pulp and paper wastewater, severe regulations have been established by different government organizations to control the maximum allowable level of contaminants in discharged effluents. These regulations, with the growing public awareness, force industries to treat their effluent to the required level before discharging to the environment (Pokhrel and Viraraghavan, 2004).

1.2 Objectives

The main objective of the present work is to develop a sustainable process to reduce CO_2 emissions by its bioconversion into methane using the anaerobic treatment of wastewater. This conversion is based on the final step of anaerobic digestion (methanogenesis) in which methanogenic archaea convert CO_2, H_2, and simple organic molecules to methane. The aim is to inject industrial CO_2 emissions into their corresponding wastewater streams and convert the CO_2 to methane as biogas during the last step of the anaerobic treatment of wastewater. As a result of this process, CO_2 emissions can be reduced and biogas will be produced simultaneously during wastewater treatment. The experiments reported in this dissertation were conducted in two phases: 1) Batch phase and 2) Continuous phase.

1.2.1 Batch experiments

In this phase of experiments, batch tests were conducted to assess the feasibility of anaerobic treatment of pulp and paper wastewater for CO_2 removal. The results of batch tests were used to find the optimum condition for the operation of the continuous phase.

The objectives of this phase were to:

- Investigate the feasibility of the developed method for CO_2 removal using a real industrial wastewater (pulp and paper wastewater).
- Determine the efficiency of the developed method for carbon dioxide reduction.
- Determine the impact of wastewater characteristics including the COD concentration and pH on CO_2 removal.
- Evaluate the optimum operating conditions (pH and temperature) for CO_2 removal and methane generation.
- Determine the effect of CO_2 injection on COD removal and methane generation.
- Investigate the metabolism related to carbon dioxide reduction in the system.

The experiments in this phase were performed by applying different types of pulp and paper wastewater, including recycled paper and chemi-thermomechanical pulping (CTMP) wastewater.

1.2.2 Continuous experiments

The continuous phase of operation was performed following the batch tests. An upflow anaerobic sludge blanket (UASB) reactor was used to treat the wastewater. The objectives of this phase are stated below:

- To evaluate the effect of different operating conditions including the liquid pH, organic loading rate (OLR) and hydraulic retention time (HRT) on the efficiency of CO_2 and COD removal and methane generation.
- To evaluate the efficiency of CO_2 removal and methane generation in the continuous system.
- To evaluate the potential GHG reduction and the economic feasibility of the developed process by evaluating the cost and the economic viability of CO_2 reduction process as it applies to an existing wastewater treatment plant.

- To evaluate the sustainability of the developed process by applying the GoldSET software and comparing the application of three different treatment systems (aerobic, conventional anaerobic/aerobic and the developed anaerobic/aerobic) on the examined treatment plant.
- To develop a mathematical model to investigate the kinetics of the developed anaerobic digestion process and determine the kinetic parameters including the specific growth rate of biomass (μ) and half-saturation constant (K_s) for anaerobic digestion of carbon dioxide.

1.3 Thesis Outline

This thesis is organized in the following chapters:

Chapter 1 Statement of the problem, scope of the work, its application and objectives,

Chapter 2 Background information about problems associated with carbon dioxide emission, current methods applied for its reduction, anaerobic digestion as the method suggested in the present work for the reduction of carbon dioxide emission, and the associated problems with the pulp and paper wastewater,

Chapter 3 Materials and methods,

Chapter 4 Results of the experiments,

Chapter 5 Cost estimation, GHG analysis and sustainability study by applying the GoldSET software,

Chapter 6 Conclusions,

Chapter 7 Contributions and recommendations for future development of the present study,

References List of references used in this study

Appendices Calculations related to cost estimation and GHG analysis, as well as results of GoldSET software.

Chapter 2: Literature Review

2.1 Carbon dioxide: the main source of greenhouse gases

There is a balance between the amount of energy transmitted from the sun to the earth and the infrared energy radiated back to the space. This balance makes the earth temperature approximately constant over the time. Greenhouse gases (GHG) are the atmospheric gases that absorb the infrared radiation from the earth surface. The average temperature of the earth surface is around 19°C in the presence of naturally existing greenhouse gases in the earth atmosphere. As a result of human activities, the amount of GHGs increases in the atmosphere which can decrease the radiation from the earth surface and as a result make the earth temperature higher than its natural temperature. This phenomenon is called global warming (Shulk, 2007). This problem became more serious after the industrial revolution in 1750 in which human activities such as burning fossil fuels and deforestation increased the amount of carbon dioxide in the atmosphere by around 25% (Martens, 2013). As a result, the global and the arctic average temperature increased by more than 0.72°C, twice the increase during the previous century (Pachauri and Reisinger, 2007). Figure 2.1 shows the CO_2 emissions between 1965 and 2011. The rapid increase in CO_2 emission is believed to be related to human activities.

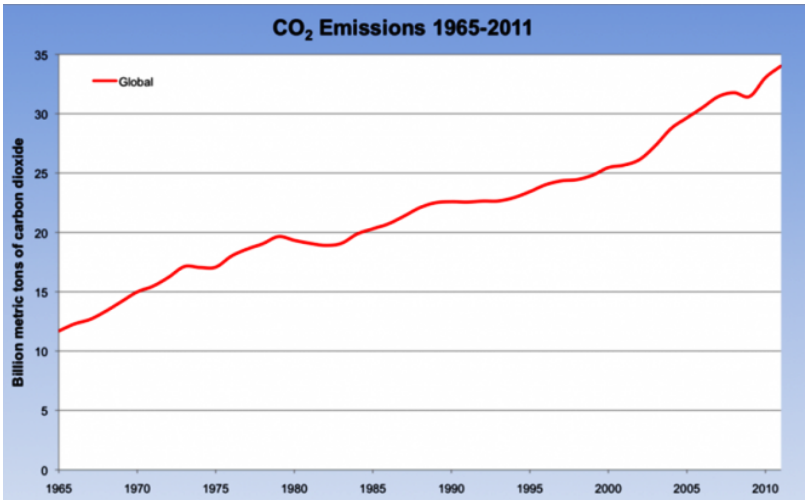


Fig. 2.1: Carbon dioxide emissions between 1965 and 2011 (Rapier, 2012)

Carbon dioxide emission accounts for the largest portion of greenhouse gases (85% in United State and 79% in Canada), and thus its concentration determines the GHG density. Other greenhouse gas emissions include methane, nitrous oxide, SF_6, HFCs and PFCs as shown in Figure 2.2 (Ramseur, 2008).

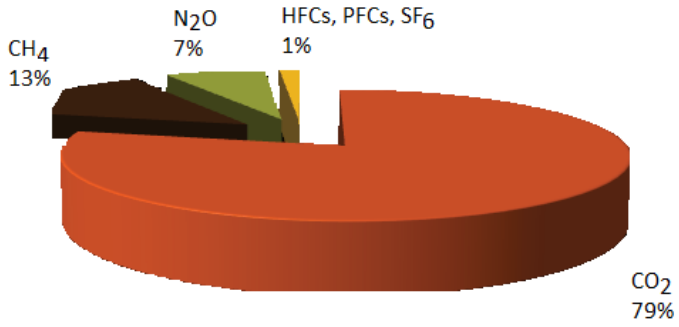


Fig. 2.2: Greenhouse Gas Sources and Sinks in Canada (Environment Canada, 2012)

Almost 98% of CO_2 emissions in the US are related to energy use. Electricity generation and transportation account for approximately 40% and 33% of CO_2 emissions in the United States, respectively (Ramseur, 2008). Figure 2.3 shows different sources of the U.S. carbon dioxide emissions, and their contribution to total CO_2 emissions.

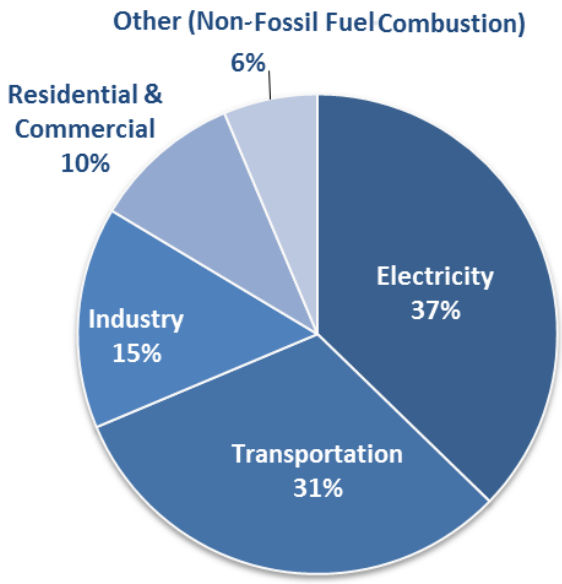


Fig. 2.3: U.S. Carbon Dioxide Emissions by Source. All emissions were estimated from the Inventory of the U.S. Greenhouse Gas Emissions and Sinks: 1990-2013 (US EPA, 2015)

Global CO_2 emissions in 2009 were 30398.42 million tons (The Guardian, 2015). A research in the University of East Anglia reported a 5.9% increase in CO_2 emissions from burning fossil fuels in 2010 and 49% increase in the last two decades. This increase corresponds to an average of 3.1% increase in annual fossil fuel emission since 2000 (Science Daily News Report, 2011). In 2010, the total emissions from fossil fuel, cement production, deforestation and other sources were 10 billion tonnes of carbon. These emissions are divided approximately in equal portions between the atmosphere, the oceans and land reservoir. As a result, the CO_2 concentration reached 389.6 parts per million in the atmosphere (Science Daily News Report, 2011).

2.1.1 Problems associated with the CO_2 emission and global warming

Global warming has significant consequences such as sea level rise which in turn can change the salinity in estuaries, decrease the continental ice sheets, and endanger the lives of people that inhabit the Low Elevation Coastal Zone which is almost 10% of the world population. It will also increase coastal erosion and coastal flooding (Mcgranahan et al., 2007; Aigner, 2011). In addition, more droughts or anomalous rainfall will be observed, and the animals, aquatic organisms and vegetation that are not able to adapt to the new climate change may become scarce or extinct. The high temperature will facilitate the growth and proliferation of insects,

resulting in the transmission of diseases (Riebeek, 2010). A research report in Science daily news shows that high concentrations of CO_2 can affect decision making. In this research, it was shown that decision making performance is considerably decreased at CO_2 levels above 1000 ppm (Science Daily, 2012).

2.2 Existing methods for the reduction of carbon dioxide

2.2.1 Natural sinks for CO_2 reduction

There are some natural sinks for CO_2 such as terrestrial vegetation as well as soil as it can trap a small portion of CO_2, geological sinks such as calcium carbonate cliffs, and the oceans based on the continuous equilibrium of CO_2 in the atmosphere and the dissolved CO_2 in water. About 90 percent of dissolved CO_2 in water exists as bicarbonate and almost 8 percent exists as carbonate (Reay et al., 2007).

After the industrial revolution, the level of anthropogenic carbon dioxide in the atmosphere has increased dramatically. As a result, many physical, chemical and biological methods are developed to enhance the capacity of natural sinks in the reduction of CO_2 concentration in the atmosphere.

2.2.2 Chemical and physical methods for CO_2 reduction

Carbon capture and sequestration (CCS) is one of the most popular techniques that captures a large amount of carbon dioxide from industrial smokestacks, compresses them into liquid and disposes them in very deep underground saline aquifers. In fact, in this method very deep saline media act as a cemetery for liquefied CO_2. This method is mostly applied for capturing carbon dioxide emissions from coal fuel-based power plants, and oil refineries (Boot-Handford et al., 2014). With the CCS technique, almost 90% of the atmospheric carbon dioxide emissions of power plants which are the major source of CO_2 emission can be captured and disposed of (Graham, 2009). The CCS process accounted for 55% reduction in carbon dioxide concentration between 2007 and 2100 (IPCC 2007).

Many technologies are applied for capturing carbon dioxide. These methods are described below (Global Climate and Energy Project (GCEP, 2005) :

Application of chemical solvents (amine solvents) for the removal of acid gas impurities from gas streams. This method is only applicable for small scale operations because it is costly. Also, it has efficiency and stability problems. An example of this application is the absorption/ stripping method, in which CO_2 is captured from the gas stream by applying a blend of an alkali salt and a secondary amine solution which increases the rate of CO_2 absorption. The solvent will then be separated from the gas in a stripper and can be reused (Rochelle and Cullinane, 2007). In another process a liquid containing an anion with a carboxylate function is applied as a selective adsorbent for CO_2 removal from a gas stream (Chinn et al., 2005)

- **Physical absorption** by applying physical absorbents or a mixture of physical/ chemical absorbents. This method involves the absorption and desorption of gas under specific temperature and pressure. This method has a higher capacity for CO_2 capture compared to the chemical absorption.
- **Physical adsorption** by applying a regenerable physical adsorbent such as activated carbon or by applying a membrane separation processes. The applicability of this method depends on the affinity of CO_2 to the material surface without formation of a chemical bond.
- **Chemisorption** by applying a metal oxide air separation or dry chemical absorbents. In this method gas molecules are chemically bound to the surface of some materials. Chemisorbents are composed of an inert substrate that is covered by an active surface.
- **CO_2 mineralization** in which some minerals create stable, thermodynamically favoured chemical bonds with CO_2 in the gas stream. As an example for application of this method, carbon dioxide is used for the synthesis of chemicals for technological applications, whereby the applied chemicals act as an artificial sink for carbon dioxide. This method is now used for just a few applications, mostly for the synthesis of urea, in which the amount of converted CO_2 is approximately equal to 110 Tg per year (Reay et al., 2007).

  The atmospheric CO_2 is in permanent equilibrium with the oceanic CO_2. The transformation of CO_2 isolated from the atmosphere to insoluble $CaCO_3$ minerals followed by the transfer of precipitates to the sea bottom is another method for the removal of CO_2 (eq. 2.1). As a result of this precipitation, water can absorb more CO_2 from the atmosphere [8].

$$Ca^{2+} + 2HCO_3^- + OH^- \rightarrow CaCO_3(s) + CO_3^{2-} + 3H^+ + H_2O \quad (2.1)$$

- **Phase Separation method** such as cryogenics. In this method, different gases in a gas mixture are separated in different phases based on their difference in the boiling temperature values.

The disposal option of CO_2 by direct injection is another method for its reduction. It can be divided into the geological injection and oceanic injection. Enhanced oil recovery (EOR) is an example of geological injection. In this method, CO_2 is injected into an oil reservoir and becomes miscible with the oil and makes its extraction easier (Stewart and Hessami, 2005).

The use of carbon dioxide for the neutralization of alkaline wastewater is another method for its safe disposal. In this method, the wastewater acts as a chemical absorbent. This is an economical way to neutralize this type of wastewater that reduces the consumption of acids (Gaur, 2009). In another process an electrolytic CO_2-removal device for anion analysis of a liquid sample is used. The device includes CO_2-permeable tubing in a basic chamber. Anion exchange membranes are on opposite sides of the basic chamber, with electrodes are on the outside of the membranes" (Riviello, 2014). Another method is the CO_2 emission trading system in which according to the Kyoto protocol, countries can distribute emission allowance to private sector emitters. Those emitters who reduce their emissions can sell their allowance to the emitters who emit more CO_2 than their allowance (Reay et al., 2007).

2.2.3 Biological method for the reduction of CO_2

A certain group of microorganisms can use carbon dioxide as a source of carbon through several autotropic pathways. These microorganisms that are capable of CO_2 fixing can be used for biological reduction of atmospheric CO_2 (Saini et al., 2011). Two examples of this biological fixation of CO_2 include biofixation through microalgae photosynthesis and biofixation by applying *Chlamydomonas sp.* in a tubular photobioreactor (Hadiyanto et al., 2012). Biological conversion of carbon dioxide gas to carbonates which can be used as building materials has been done by using ordinary baker's yeast. This process has the potential to convert one pound of CO_2 to two pounds of carbonate (Belcher and Barbero, 2010).

The photosynthetic conversion is a natural process that can fix carbon dioxide by using bacteria in a controlled environment such as a bio-reactor. In this method, the activity of microorganisms was stimulated by light in the bioreactor and useful by-products are produced as a result of CO_2 fixation (Stewart and Hessami, 2005). In a biological study by applying Fe (III)-reducing bacteria in conjunction with metal containing fly ash and lime, CO_2 was converted into sparingly soluble carbonate minerals such as calcite ($CaCO_3$) and siderite ($FeCO_3$). In this process, fly ash was stabilized into carbonate solid conglomerates that could potentially be useful as fill materials or road construction aggregates (Roh et al., 2000).

Hybrid copper-gold nanoparticles can turn CO_2 into methane or methanol in an electrochemical reaction. In this method, copper was used as an electrode, and stimulated by voltage it acts as a strong catalyst and can turn CO_2 into methane or methanol in an electrochemical reaction. Nanoparticles of gold make copper more resistant to corrosion and oxidation (Chu, 2012).

In another method, clusters of titanium oxide nanotubes coated with a catalyst were used to convert the captured CO_2 and water to methane. At Penn State University, a team of researchers worked on this method of turning the captured CO_2 into methane. The power source for this process is sunlight, so the cost of this conversion in not significantly high (Boysen and Muir, 2011). Examples of biological methods to reduce carbon dioxide emissions in power plants include photosynthetic systems with cyanobacteria or microalgae (Maeda et al., 1995; Taguchi, et al. 1997) and bio-electro methods (Kuroda and Watanabe, 1995).

2.2.3 Anaerobic treatment approach for the reduction of CO_2

An alternative biological process with the potential to remove carbon dioxide is anaerobic digestion. In the final step (methanogenesis), simple organic molecules including short-chain fatty acids along with carbon dioxide and hydrogen, are converted to biogas as shown in Figure 2.4. There are two potential mechanisms for CO_2 removal by anaerobic treatment. One mechanism is the enhancement of acidogenic and acetogenic stages in which the additional CO_2 from the enriched wastewater can combine with reducing agents and produce acetic acid and increase VFA concentration which increases methane production. The other mechanism is simulation of CO_2 reduction by hydrogenotrophic methanogens in which the additional CO_2 from enriched wastewater increases the substrate concentration for hydrogenotrophic

methanogens. Therefore, it is possible to simulate these steps and provide conditions to convert carbon dioxide to biogas using methanogens (Fernandez et al., 2012).

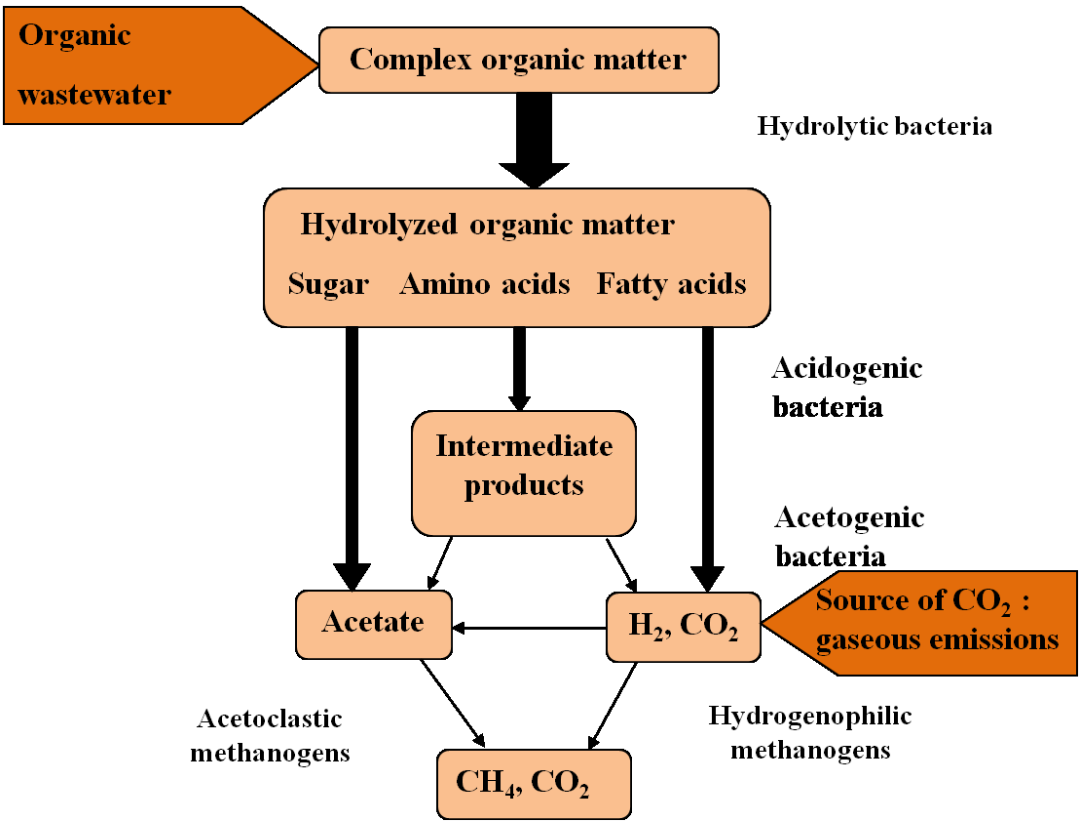


Fig. 2.4: Schema of the anaerobic degradation process

Several studies have been done on application of anaerobic digestion for CO_2 removal. The potential of anaerobic digestion for CO_2 uptake was first reported by Sato and Ochi (1994). They injected CO_2 periodically into the anaerobic digester of sewage sludge and reported up to 30% increase in the specific methane yield which is the volume of CH_4 produced per mass of VS added (Sato and Ochi, 1994). Salomoni et al. (2011) reported a 25% increase in methane generation and 112% increase in methane generation rate in pilot two phase anaerobic digestion of sewage sludge when the wastewater was continuously enriched with CO_2. The CO_2 was captured from the sludge incineration flue gas by an alkaline solution in a scrubber and after regeneration was sent to the two phase anaerobic digestion. Fernandez et al. (2014) studied the effect of CO_2 uptake on food waste and sewage sludge in anaerobic batch tests and reported 11–16% increase in biogas for food waste and 96–138% for sewage sludge over the first 24 h. They reported 3–11% CO_2 reductions for food waste and 8–34% for sewage sludge. The feasibility of

conversion of CO_2 to methane was evaluated using synthetic methanogenic media in the presence of different VFAs by Alimahmoodi and Mulligan (2008). They suggested the potential uptake of 69–86% CO_2 when dissolving this gas in the influent to an UASB reactor. In their study, CO_2 was injected prior to the start of the anaerobic process (Alimahmoodi and Mulligan, 2008). In another study, CO_2 was applied as a co-substrate for anaerobic treatment of high concentration of methanol in wastewater. In this work, an increase in the methanol removal from wastewater and CO_2 removal were achieved at the same time (Argelis Avila Molto, 2007). The above mentioned literature was focused on application of anaerobic digestion for CO_2 removal, while there was no study done focusing on the anaerobic treatment of wastewater for CO_2 removal. Moreover, there is a lack of study on the effect of different operating conditions (temperature, and pH) on the efficiency of CO_2 removal by anaerobic treatment which is evaluated in the present study.

2.2.4 Using other sources of energy instead of fossil fuel energy

The main sources of energy in the world are fossil fuel, nuclear energy and renewable sources such as wind, water and solar energy. Fossil fuel is a non-renewable source of energy and its burning is the main reason for the increase in the concentration of carbon dioxide in recent years and the global warming phenomenon. But it is still the main source of energy and contributes to almost 82% of energy consumption in the world (World Energy Council, 2013).

But is it possible to replace fossil fuel with other sources of energy such as nuclear energy or renewable energies?

To answer this question, it should be mentioned that although nuclear energy emits less atmospheric pollutant in comparison with fossil fuel burning, it is a non-renewable source of energy and it has many problems associated with its application such as difficulty in waste management, and limited life of nuclear plants.

These problems limit the application of nuclear energy as a source of energy. Other sources of energy including wind, water power, and solar (WWS) are renewable sources, but there are many barriers on their application such as desired geological and climate conditions and access to a large space. Most barriers in the application of renewable energy resources are social and political (Jacobson and Delucchi, 2011).

2.3 Anaerobic treatment method

Anaerobic treatment differs from aerobic treatment in that no aeration is applied. This method is very efficient for the treatment of highly concentrated wastewaters (over 1,500 mg COD/l) with a low to moderate level of nitrogen. The wastewater discharge from many industries such as beer and soft drink producing factories, pulp and paper industries and food producing companies can be treated by anaerobic processes (Beers, 2010). The anaerobic treatment process offers many advantages compared to aerobic treatment processes that have caused many treatment plants to switch from their conventional aerobic treatment to anaerobic treatment. Table 2.1 shows the comparison between aerobic and anaerobic treatment methods (Grady et al., 1999; Chan et al., 2009; Metcalf and Eddy, 2003).

Table 2.1: Comparison between aerobic and anaerobic treatment methods

Feature	Aerobic	Anaerobic
Reactor size	Bigger	Smaller
Susceptibility to toxic material and temperature	low	High
Organic removal efficiency	High	High
Effluent quality	Excellent	Moderate to poor (post-treatment process may be needed)
Organic loading rate	Moderate	High
Sludge production	High	Low
Nutrient requirement	High	Low
Alkalinity requirement	Low	High for certain industrial waste
Energy requirement	High	Low to moderate
Start up time	2-4 weeks	2-4 months
Odor problem	Less	More
Biogas generation	No	Yes

In anaerobic processes, each kilogram of COD removed produces 1.16 kWh of electricity from methane. Furthermore, no aeration is needed, thus less energy is required. On the other hand, the aerobic process consumes 0.5 – 0.75 kWh of energy for every kilogram of COD removed

(Shihwu Sung, 2008). Other advantages of anaerobic processes include lower production of sludge, approximately 20% of that produced by aerobic treatment processes, resulting in savings that would be spent on the treatment and disposal of sludge (Shihwu Sung, 2008). The biogas produced by anaerobic processes is generally composed of 48–65% methane, 36–41% carbon dioxide, <1% to 17% nitrogen, <1% oxygen, 32–169 ppm hydrogen sulphide, and traces of other gases (Rasi et al., 2007). The anaerobic treatment process is applicable by using different types of reactors, but the upflow anaerobic sludge blanket (UASB) is the most predominant technology. Many other technologies have been developed as derivatives of the UASB technology at an increased efficiency. For example, the expanded granular sludge bed reactor (EGSB) is designed for higher loads (Frankin, 2001).

In the pulp and paper industry, anaerobic treatment is usually used for non-toxic, readily biodegradable effluents. The application of anaerobic treatment for the discharge of chemical pulping process which is less biodegradable is limited and is usually done by UASB reactors. These reactors usually work with granular sludge which is more resistant to toxicity (Jantsch et al., 2002).

The anaerobic treatment or anaerobic digestion process occurs in four steps (Figure 2.4) in which different types of microorganisms break down biodegradable material in the absence of oxygen. Initially, the bacteria break down the insoluble organic polymers to simpler products such as sugars and amino acids during the hydrolysis stage. During the acidogenesis stage, acidogenic bacteria use the products of the first stage to produce carbon dioxide, hydrogen, ammonia, and organic acids. In the third stage, acetogenic bacteria convert the resulting organic acids to acetic acid, carbon dioxide, hydrogen, and ammonia. Finally, in the last stage (methanogenesis), methanogenic bacteria consume the resulting products of previous stages to produce methane and carbon dioxide (Tabatabaei et al., 2010).

Traditionally, anaerobic treatment has been performed in a single stage system and all 4 steps were done in one reactor. This system for treatment is easy to build and maintain, but has lower performance compared to the multi-stage systems. Multi-stage systems are designed based on the difference in optimum environmental conditions for acidogenesis and methanogenesis processes. As a result, in recent years the application of two-stage anaerobic treatment has become more favorable in which the hydrolysis/acidification processes are separated from the

acetogenesis/methanogenesis processes. This system is more stable because of less fluctuations in the organic loading rate and a higher performance (Ward, 2008).

2.4 Methanogenesis and types of methanogens

Methanogens are anaerobic bacteria that generate methane as part of their energy metabolism. They originate from the domain Archaea and they usually flourish in mud deposits, garbage landfills, in poorly drained soils, in the rumen of ruminants and intestinal tract of animals and humans.

Methanogenesis leads to the production of approximately one billion tons of methane per year (Cohen, 2011). The reaction for methane production is:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O + \text{energy (in the form of ATP)} \qquad (1)$$

The produced energy as ATP during methanogenesis will be consumed as a source of energy for methanogens. This energy is produced as a result of the reduction of methyl group by electrons from electron donor groups such as H_2, formate, methanol, methylamines or acetate, and in some rare cases, from ethanol or propanol. Most methanogens can only reduce CO_2 to methane, but one group of methanogens (methanosarcinales) can convert other compounds such as methanol, and acetate to methane as well (Cohen, 2011).The reduction of CO_2 to methane is shown in Figure 2.5. This conversion happens by the application of six coenzymes via the formyl, methenyl, methylene and methyl stages.

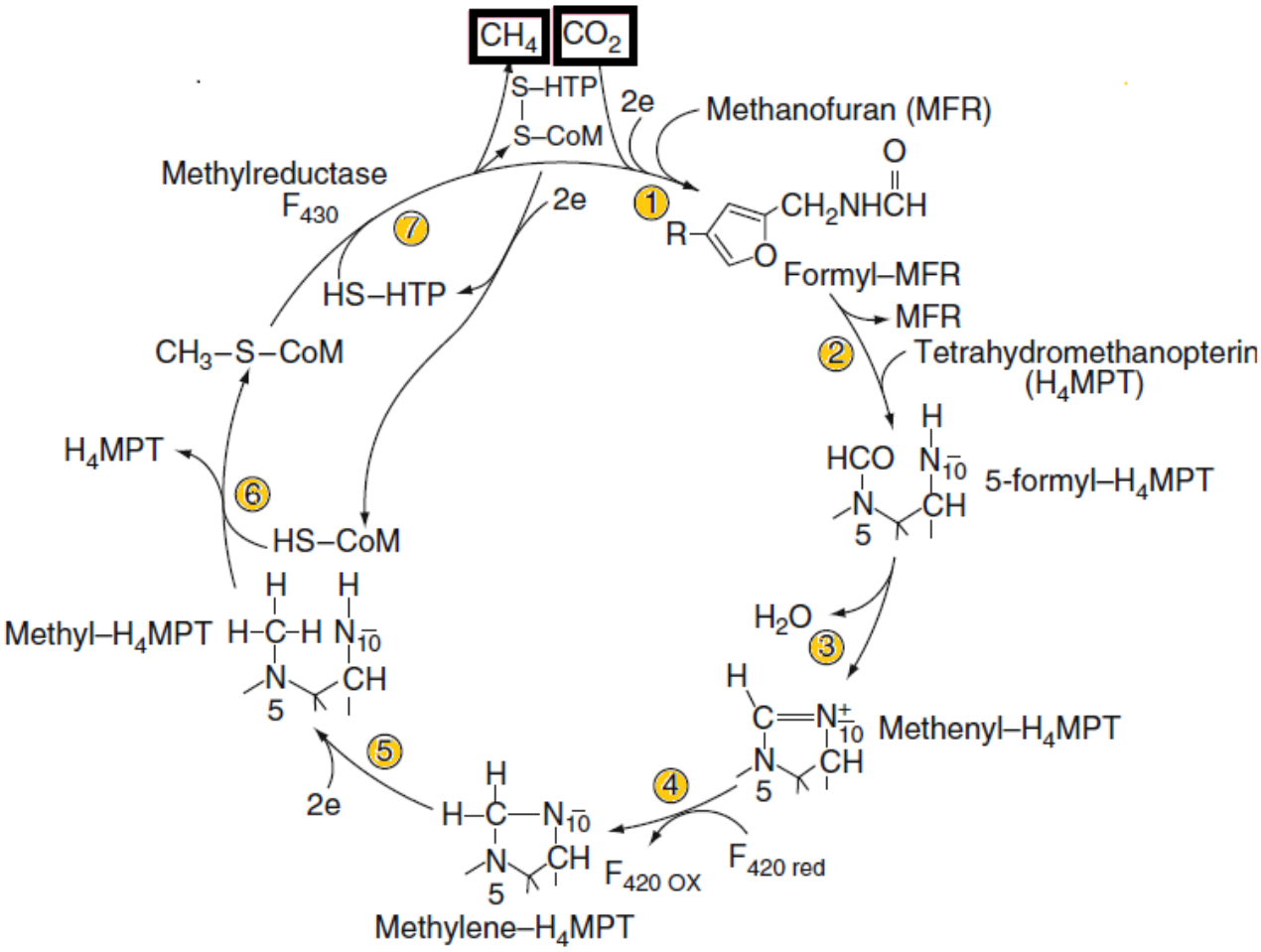


Fig. 2.5: Methanogenic pathway (adapted from Cohen, 2011).

Methanoarchaea exist in a variety of anaerobic environments from moderate to extreme temperatures (from 0ºC to 110ºC) and in the presence of salinity. The *methanoarchaea* thrive in anaerobic environments where O_2, sulfate, oxidized metals, and nitrate are absent because they are better electron acceptors than CO_2 and will be consumed more easily by the reducing bacteria (Issazadeh et al., 2013). The *methanoarchaea* are divided in to five different orders and thirty-one genera which are shown in Table 2.2.

Table 2.2: Taxonomy of the methane-producing Archaea (Hedderich and Whitman, 2006).

Order	Genus	Morphology	Major energy substrates	Optimum temperature (°C)
Methanobacteriales	*Methanobacterium*	Rod	H_2, (formate, alcohols)	37–45
	Methanothermobacter	Rod	H_2, (formate)	55–65
	Methanobrevibacter	Short rod	H_2 (formate)	37–40
	Methanosphaer	Coccus	H_2+ methanol	37
	Methanothermus	Rod	H_2	80–88
Methanococcales	*Methanococcus*	Coccus	H_2, formate	35–40
	Methanothermococcus	Coccus	H_2, formate	60–65
	Methanocaldococcus	Coccus	H_2	80–85
	Methanotorrts	Coccus	H_2	88
Methanomicrobiales	*Methanomicrobium*	Rod	H_2, formate	40
	Methanoculleus	Irregular coccus	H_2, formate (alcohols)	20–55
	Methanofollis	Irregular coccus	H_2, formate (alcohols)	37–40
	Methanogenium	Irregular coccus	H_2, formate (alcohols)	15–57
	Methanolactnia	Rod	H_2 (alcohols)	40
	Methanoplama	Plate or disc	H_2, formate (alcohols)	32–40
	Methanospirillum	Spirillum	H_2, formate (alcohols)	30–37
	Methanocorpusculum	Small coccus	H_2, formate (alcohols)	30–40
	Methanocalculus	Irregular coccus	H_2, formate	30–40
Methanosarcinales	*Methanosarcina*	Coccus, packets	Methanol, $MeNH_2$, (H_2, Ac, DMS)	35–60
	Methanococcoides	Coccus	Methanol, $MeNH_2$	23–35
	Methanohalophilus	Irregular coccus	Methanol, $MeNH_2$	35–40
	Methanohalobium	Flat polygons	Methanol, $MeNH_2$	40–55
	Methanolobus	Irregular coccus	Methanol, $MeNH_2$ (DMS)	37
	Methanomethylovorans	coccus, packets	Methanol, $MeNH_2$ DMS,MT	34–37
	Methanomicrococcus	Flat polygons	H_2 + Methanol, H_2 +$MeNH_2$	39
	Methanosalsum	Irregular coccus	Methanol, MeH_2, DMS	35–45
	Methanosaeta	Rod	Ac	35–60
Methanopyrales	*Methanopyrus*	Rod	H_2	98

There are three different pathways for methanogenesis which produce methane from CO_2 and H_2 or from acetate or methanol. These pathways are shown in Fig 2.6. In all pathways, methyl-coenzyme M (CH_3-S-CoM) is a central intermediate which is converted to a hetero disulfide and methane. Hetero disulfide then acts as the final electron acceptor and is converted to coenzyme M and coenzyme B.

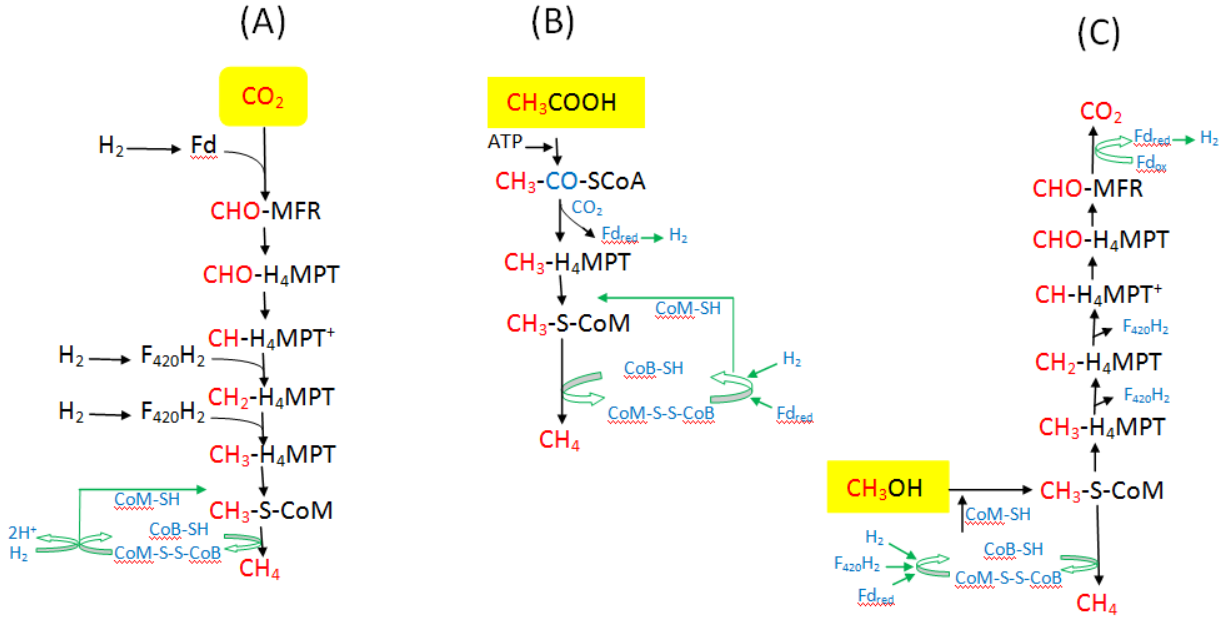


Fig. 2.6: Three different pathways for methanogenesis. Schematic of methanogenesis from H_2/CO_2 (A), acetate (B) and methanol (C) (Hedderich, and Whitman, 2006)

2.5 Pulp and paper wastewater

Pulp and paper production is a very water demanding industry. It consumes up to 35 m^3 of fresh water for production of each tonne of paper and produces at least 30 m^3 wastewater discharges per tonne of manufactured pulp (Tabatabaei et al., 2010). It is the largest consumer of process water and after the chemicals and metals industries is the third largest consumer of energy (U.S. Department of Commerce, 2000; U.S. Department of Energy, 2000). The pulp-and-paper industry is one of the leading industries in energy consumption and GHG emissions. It is the second largest consumer of energy in Canada after the mining and oil and gas extraction (Statistics Canada, 2010). A study in Japan reported electricity consumption in the amount of 1130 kWh/paper ton in an integrated fine paper mill (UNIDO and MITI, 1993). In another

report by ABB pulp and paper, a Swedish pulp mill consumed 635 kWh per pulp ton (ABB, 2008). Nygaard (1997) classified the energy requirement for different pulping methods, as presented in Table 2.3 (adt = air dried ton).

Table 2.3: Total Energy Consumption for Different Pulp Facilities Excluding Paper Machines

	Electrical Power(kWh/adt)	Process Heat(kWh/adt)	Total(kWh/adt)
Kraft	560	2500	3060
TMP/CTMP	3000	200	3200
Deinked pulp	600	220	820

In this industry, the wastewater results from different processes such as paper making, wood pulping, and deinking with the average COD of 11 kg/l. Among these processes, pulping is the main source of chemical and toxic substance discharge to the environment. Pulp is a lignocellulosic fibrous material prepared during pulping process by removing lignin from the wood. By this process wood chips are separated into individual cellulose fibers (US EPA, 2010). The most common pulping processes are mechanical pulping, Kraft and sulphite chemical pulping, chemo-mechanical pulping (CMP), recycle pulping, thermo-mechanical pulping (TMP), and chemo-thermomechanical pulping (CTMP) (Pokhrel and Viraraghavan, 2004). The chemicals and pollutants vary depending upon the type of the pulping process that is applied. In mechanical pulping, physical energy such as shredding is applied to separate pulp fibers from raw wood. In chemical pulping on the other hand, the raw material is cooked in a chemical solution under elevated temperature and pressure to extract pulp fibers. Chemical pulping is carried out in alkaline (Kraft process) or acidic (Sulfite process) media. The Kraft process is the most widely used process which is done with addition of NaOH and Na_2S as chemicals. Disadvantage of this process is the odor problem, based on production of thiols and sulfides. In sulphite process H_2SO_3 and HSO_3^- are added in order to dissolve lignin. (Pokhrel and Viraraghavan, 2004) Recycled pulping, uses the previously manufactured products such as cardboard as the raw material and recover them by applying hydration and agitation (US EPA, 2010).

The effluent from the paper industry is a moderate to high strength wastewater and contains a high concentration of lignin, resins, tannins, and chlorinated compounds, and therefore it is usually toxic and resistant to biodegradation. The combination of aerobic and anaerobic treatment are good choices for its treatment. UASB is the most common anaerobic treatment method, while activated sludge and aerated lagoons are the most common aerobic treatment methods, traditionally used in the pulp and paper industry (Mahmood and Elliot, 2006; Tezel et al., 2001).

Anaerobic biological treatment processes by using granular methanogens, which can tolerate more toxicity, is usually applied for the treatment of this toxic wastewater and can remove a large portion of biodegradable COD and sulphur from it. The dominant methanogens during the operation of anaerobic treatment of pulp and paper wastewater in a UASB reactor are *Methanosarcina spp.* and *Methanosaeta spp.* which play a significant role in the degradation of highly chlorinated compounds. Other dominant microorganisms in the anaerobic treatment of pulp and paper are *Methanobacterium sp.,* sulfate-reducing bacteria and syntrophic fatty acid-oxidizing microorganisms (Tabatabaei et al., 2010).

Based on the toxicity of pulp and paper wastewater, its discharge to surface waters without treatment introduces a large amount of toxic substances to the water which endangers the aquatic life and affects the terrestrial ecosystem. It also leads to the formation of scum, thermal impact, slime growth, change in water color, and loss of aesthetic beauty in the environment which demonstrate the high importance of treatment for this wastewater (Pokhrel and Viraraghavan, 2004).

2.6 Cost estimation

Cost analysis is carried out to predict if the project is economically feasible for capital investment. This decision is made based on the net profit which is defined as equation 2.1. If the net profit is negative, the project is not economically feasible (Peters and Timmerhaus, 1991).

$$Net\ profit = Total\ income - all\ expenses \quad (2.1)$$

The total costs of the process consist of investment cost (capital cost) and operation and maintenance cost. Capital costs includes site characterization, hydrogeological investigation, construction (excavation, cost of building the treatment units), mechanical instruments (blowers

and sludge dewatering equipments, and clarifier scraper), footprint, electrical connections, piping, transportation, and others (engineering, supervising and consulting) (Buyukkamaci and Koken, 2010; Tsilemou and Panagiotakopoulos, 2006).

Operation and maintenance cost include laboratory tests, electricity, coagulant consumption, sludge disposal and transportation, labor and supervision (Tsilemou and Panagiotakopoulos, 2006). In order to find the unit treatment cost, the capital cost should be considered for the life of project (for example 30 years for anaerobic treatment). The monthly investment (capital) cost are added to the operational and maintenance costs and the overall cost of project is divided by the volume of treated wastewater (Buyukkamaci and Koken, 2010). In order to determine the cost in the present time based on the original cost, an index value is used as reported in equation 2.2 (Peters and Timmerhaus, 1991). The index value is the statistical measure of change in an economy or a securities market:

$$Present\ cost = original\ cost \left(\frac{index\ value\ at\ present\ time}{index\ value\ at\ time\ original\ cost\ was\ obtained}\right) \quad (2.2)$$

2.6.1 Treatment costs:

Numerous literature studies have been conducted to determine the cost of different processes in the pulp and paper treatment operations. Most available data are from mathematical models, while only a small amount of data exists from case studies, which are presented in this chapter. Figure 2.7 shows the distribution of investment (capital) and operational costs for pulp and paper wastewater treatment plants in Turkey using UASB reactor followed by conventional activated sludge (CAS) with no tertiary treatment. This case study reports that engineering, supervising and consulting together consume 15% of construction costs while transportation accounts for another 15% of construction costs. The cost for footprint is 85\$/m^2, electricity is 0.125\$/kWh, sludge disposal is 17\$/m^3, and coagulant consumption is 0.23\$/kg for lime, 0.28\$/kg for alum, and 5.65\$/kg for polymer. The annual maintenance cost was estimated to be around 3% of the capital cost (Buyukkamaci and Koken, 2010).

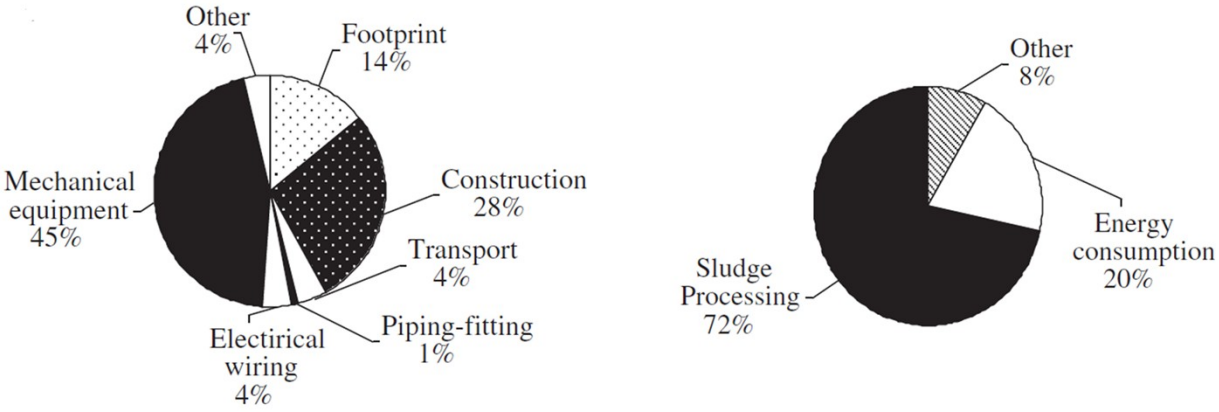


Fig. 2.7: Distribution of capital (left) and operational costs (right) for high strength pulp and paper WWTPs in Turkey

Buyukkamaci and Koken (2010) compared the capital cost and operational and maintenance costs of the pulp and paper industries in Turkey with different types and concentrations of pollutants, and reported the treatment cost per unit volume of wastewater at different wastewater flow rates. Table 2.4 presents the data related to high strength pulp and paper wastewaters

Table 2.4: Results for high strength pulp and paper wastewaters

	Wastewater Flow (m^3 day^{-1})	3000	4000	5000	6000	7000	8000	9000	10000
UASB + Conventional AS	Investment ($)	891861.7	1114069	1422907	1601334	1840617	2055500	2308961	2498042
	Operational ($\$ m^{-1}$)	55633.04	80786.09	100026.1	120304.3	135552.2	158449.6	173684.3	188921.7
	Maintenance ($\$ m^{-1}$)	2200	2747.826	3509.565	3949.565	4539.13	5069.565	5694.783	6160.87
	Unit treatment cost ($\$ m^{-3}$)	0.70	1.01	1.25	1.50	1.69	1.97	2.16	2.35

* $\$ m^{-1}$ = $\$ month^{-1}$.

2.6.2 Energy Cost

In Canada, the average price of electricity (kWh) for 400,000 kWh/month consumption with the power demand of 1000 kW is 41,995.38$/month based on 0.105$/kWh, for 10,000 kWh/month consumption with the power demand of 40 kW is 1,237.63$/month based on 0.124$/kWh, and for 100,000 kWh/month consumption with the power demand of 500 kW is 13,612.28 $/month which is based on 0.136$/kWh (Hydro Quebec, 2013).

2.7 Greenhouse gas Analysis

GHG emissions from WWTPs depend on the applied treatment methods. In the pulp and paper industry, the GHG emissions consist of CO_2, methane and nitrous oxide. Other emissions are negligible. The first step in the estimation of GHG emissions is to determine the emission sources. The sources of GHG emissions in WWTPs are classified as on-site and off-site emission sources. The on-site GHG emissions originate from the WWTPs due to biological processes (liquid and solid treatment processes), as well as biogas and fossil fuels combustion. Off-site GHG emission are related to the production and transmission of fuels and chemicals for on-site use, as well as off-site generation of electricity (Yerushalmi et al., 2013).

2.7.1 On-site GHG emissions

The on-site emissions of CO_2, CH_4, and N_2O are related to the following processes inside the WWTPs:

- CO_2 , and CH_4 generation from soluble organic substrate removal (BOD removal)
- N_2O from degradation of nitrogen compounds in wastewater (WW), along with nitrification and denitrification processes
- CO_2 from endogenous respiration of biomass in bioreactor
- CO_2 from combustion of the produced biogas in anaerobic bioreactor and sludge digester
- CH_4 from the leakage of biogas produced in anaerobic bioreactor and sludge digester
- CO_2 from biomass combustion or sludge landfilling
- CH_4 and N_2O from sludge digestion or sludge landfilling
- CO_2, CH_4, and N_2O from fossil fuels combustion such as natural gas or diesel.

Carbon dioxide emission from the burning of biomass is not included in the GHG emissions. The carbon in biomass originates in the atmosphere and is called "carbon neutral". The burning of biomass releases CO_2 to the atmosphere again. In this case the biomass- derived CO_2 is reported separately. However methane and nitrous oxide from biomass combustion are usually included in GHG calculations, as they don't participate in the atmospheric CO_2 recycling process. (NCASI, 2005).

In the case of biomass landfilling, the only GHG emission based on the most widely accepted protocols is methane. CO_2 is considered carbon neutral and nitrous oxide production is assumed to be negligible (NCASI, 2005). Methane and nitrous oxide emissions from fossil fuel combustion are negligible compared to CO_2 emission. Therefore, many inventories do not address their generation (NCASI, 2005). N_2O emission from the treatment plants is assumed to be small and happens after wastewater discharge (NCASI, 2005). Incomplete nitrification and denitrification processes can cause N_2O emission. According to IPCC, this emission is assumed to be equal to 0.5% of the wastewater nitrogen content (Kampschreur et al., 2009). Commonly, 95% of the produced biogas in anaerobic treatment is recovered for energy use and 5% leaks to the atmosphere during the collection and recovery processes (Bani Shahabadi et al., 2009; Leilieveld et al.; 2005, Ashrafi, 2012).

2.7.2 Off-site GHG emissions

The off-site GHG emissions are related to the production and transmission of fuel to the treatment plant and off-site electricity production. These emissions are calculated based on the required energy in the plant. A value of 0.94 kg CO_2 /kWh is assumed for the required external energy production (based on the efficiency of a coal-burning power plant) (Bridle et al., 2008).

2.7.3 Energy

There are three sources of energy production for the treatment plant:

- Recovered biogas from anaerobic treatment and sludge digestion
- Electricity (used for mixing, aeration, pumps, and other electrical devices)
- Fossil fuel (as a source of heat and energy)

The important energy consumers in WWTPs are:

- Heating of the digester and bioreactor influent.
- Energy consumption for mixing, aeration, pumps, and other electrical devices.
- Heat losses from the reactors, digester, and piping.

The initial temperature of wastewater entering the treatment plant has a great impact on the required energy of the treatment plant. Pulp and paper wastewater usually has a relatively large temperature range (20 – 70°C) (Wising, 2003). If the applied process for pulp production contains heating, such as CTMP (Chemo Thermo Mechanical Pulping), then the wastewater that enters the treatment plant has a higher temperature and requires less energy for mesophilic or thermophilic anaerobic treatment. Therefore the treatment plant requires less energy and produces a low emission of GHG.

2.7.4 Biogas Recovery

The recovery of biogas generated from anaerobic treatment and its use as an energy source has a significant impact on GHG emissions. The combustion of biogas may cover the entire energy required in the WWTP while creating emissions credit. In a case study performed by Keller and Hartley (2003), by applying anaerobic treatment before aerobic treatment and by recovering biogas, the GHG emission was reduced from 2.4 kg CO_2/(kg COD removed) for fully aerobic treatment to 1kg CO_2/(kg COD removed) for primarily anaerobic process (Keller and Hartley, 2003). In another study, Bani Shahabadi et al. (2010) developed a mathematical model to predict GHG emissions in a wastewater treatment system that used anaerobic process before aerobic process. They reported that biogas recovery and use for energy generation reduced GHG emissions by 1023 kg CO_2e/d from a total of 7640 kg CO_2e/d when treating a wastewater at 2000 kg BOD/d. In addition, emissions credits equal to 34 kg CO_2e/d were created (Bani Shahabadi et al., 2010).

2.7.5 Global Warming Potential (GWP)

To calculate the total GHG emission from WWTPs, the Global Warming Potential (GWP) is used which is a parameter that enables comparison of the potential climate impact of different GHG emissions (Table 2.5). Global Warming Potential compares the integrated radiative forcing over a specified period (e.g., 100 years) from a unit mass pulse emission and is a way of comparing the potential climate change associated with emissions of different greenhouse gases (IPCC, 2007). By using the GWP, each emission can be expressed as its CO_2 equivalent and can be added to other emissions for the calculation of total GHG emission. In this study, GWP based

on 100-year horizon is used in the calculations in which 1 g methane and 1 g nitrous oxide are equal to 21 and 310 g CO_2e, respectively (IPCC, 2007).

Table 2.5: The GWP for different GHG emissions (IPCC, 2007)

Name	Chemical Formula	Radiative Efficiency (W m^{-2} ppb^{-1})	SAR‡ 100-yr)	20-yr	100-yr	500-yr
Carbon dioxide	CO_2	*$1.4x10^{-5}$*	*1*	*1*	*1*	*1*
Methane[c]	CH_4	*$3.7x10^{-4}$*	*21*	*72*	*25*	*7.6*
Nitrous oxide	N_2O	*$3.03x10^{-3}$*	*310*	*289*	*298*	*153*

2.8 CO_2 absorption study

In most studies carried on to determine the capacity of wastewaters to dissolve carbon dioxide, alkaline wastewaters were used. CO_2 absorption from a gaseous solution by wastewater at different temperatures, liquid and gas flow rates, and gas composition was studied by Kazemi (2013). He applied a scrubber without the addition of alkaline solution, only to increase the contact of wastewater with the CO_2 gas. The obtained results showed that temperature and gas and liquid flow rates had a low impact on the CO_2 absorption. Gas composition, however, showed a significant effect on the absorption efficiency.

Higher CO_2 absorption by wastewater was obtained at higher CO_2 concentrations in gaseous solution, lower temperatures and lower liquid flow rates. On the other hand, higher CO_2 removals from gas phase by absorption into the wastewater were reached at higher liquid flow rates, lower temperatures, and lower CO_2 concentrations in gas phase. The gas flow rate showed its effect mainly on the absorption, not on the removal efficiency.

The maximum reported CO_2 removal efficiency was 23% which was obtained when the inlet gas had 20% CO_2 content at 25°C. By increasing the temperature to 35°C at the same condition, the CO_2 removal efficiency decreased to 15.2%. As the temperature and CO_2 content of the inlet gas increased, the removal efficiency decreased. During the continuous operation, the maximum aqueous CO_2 concentrations at 25 ^oC and 35 ^oC were 11.9 and 10.3 g/L, respectively, which were obtained at the liquid flow rate of 200 ml/min and gas flow rate of 2.5 L/min. Based on this study, by applying the scrubber, the capacity of wastewater to dissolve CO_2 increases from 1.3

g/l without using scrubber (Web 1) to 11.9 g/L by using a scrubber. However the extent of absorption is lower than that obtained by using caustic solutions in the scrubber (Kazemi, 2013).

2.8.1 Scrubber

In the present research the cost estimation and GHG analysis of the developed process is done by assuming that a spray scrubber is used for capturing carbon dioxide without using any absorbents, just by increasing the contact surface. In this system, liquid droplets produced by spraying through the nozzles contact the fed gas stream inside the chamber. Spray scrubbers require low power input, however they have higher chance of clogging based on low particulate collection efficiencies. Therefore, their liquid input should have a very small particle size. This type of scrubber needs more maintenance for nozzle cleaning (Cooper, and Alley, 2011). Table 2.6 presents the absorption efficiency as well as liquid and power requirements for different spray scrubbers.

Table 2.6: Comparison of efficiency as well as liquid and power requirements for different spray scrubbers (Web 2)

Scrubber Type	Efficiency	Power Inputs *(hp/1000 cfm)*	Liquid Requirements *(gal/1000 ft^3)*
Spray-chamber	90% (+8µm particles)	0.5 - 2	1 - 20
Cyclone-spray	95% (+5µm particles)	1 - 3.5	2 - 10
Impingement	97% (+5µm particles)	2 - 3	2 - 5
Orifice	97% (+5µm particles)	0.5	2 - 4
Venturi	98% (+0.5µm particles)	3 - 12	3 - 15

The annualized cost for using scrubbers is estimated to range from \$3000-\$172,000 per m^3 /sec gas flow rate (Web 3). EPA air pollution control cost manual (2002) reported the cost of applying a venturi wet scrubber with conventional design under typical operating conditions, by assuming that the inlet loading is approximately 7g/sm^3 (3g/scf) and the control efficiency is 99% (Table 2.7). To calculate these costs, costs of pumps and treatment/disposal of solvent is not

considered in this cost estimation. For the large units costs per m^3 flow rate are much lower than small units (EPA, 2002).

Table 2.7: Cost of applying a venturi wet scrubber with conventional design (2002)

Capital cost	$5300 to $45000 per *$sm^3$/sec ($2.5 to $21 per scfm)
Operation and maintenance cost	$9300 to $254000 per sm^3/sec ($4.4 to $120 per scfm), annualy
Annualized cost	$12000 to $409000 per sm^3/sec ($5.7to $193 per scfm), annualy
Cost effectiveness	$77 to $2600 per metric ton ($70 to $2400 per short ton),annualized cost per ton per year of pollutant controlled

* sm^3 = standard cubic meter

2.8.2 Carbon offset

Every year a large amount of GHGs are emitted to the atmosphere. For example, Canada produced 728 $MtCO_2e/y$ in 2012 (TWBG, 2014). There are some policies that help countries to manage and reduce their GHG emissions. A carbon offset is a credit given to one party for reduction of CO_2 or other GHGs. This credit can be purchased and used by another party in order to compensate or offset their emissions made elsewhere.

Carbon offsets are typically measured and sold in metric tons of carbon dioxide equivalent (CO_2e). This trade is through the government, financial institutions, international brokers, online retailers and trading platforms. Carbon offset trading could be a win-win transact for both parties. The seller, benefits from selling the credit because it makes their business economically viable. On the other hand, for buyers, buying the CO_2e credit is usually cheaper than mitigating the emission of their GHG production (Carlson et al., 2009). Figure 2.8 shows the effect of carbon offset on climate. It is estimated that the carbon credit market, transacted over CAD$139 billion in 2008 which was double than its value in 2007 (Carlson et al., 2009). According to Topo Geo in 2012, the value of Carbon Credit (CC) was U.S. $ 6.50 / ton CO_2e, while the CC value per hectare was U.S. $1,300.00 (Topo Geo, 2012).

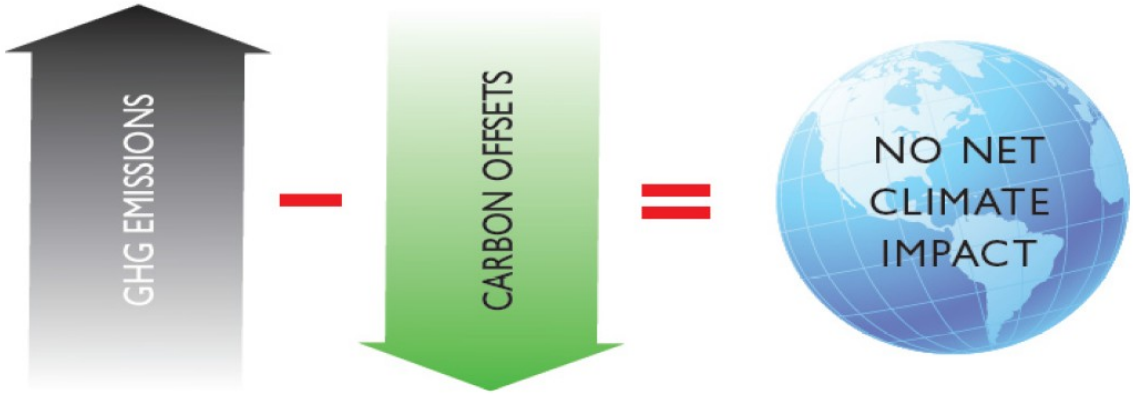


Fig. 2.8: Effect of carbon offset on climate impact. (Carlson et al., 2009)

Biological treatment of wastewater has the potential to attain revenue as carbon credit for the wastewater treatment plant. Methane generated in anaerobic treatment could be collected and used as a renewable source of energy. Combustion of methane instead of fossil fuel offsets the CO_2 emission from fossil fuel. On the other hand, the CO_2 generated as a result of methane combustion is not a GHG and is a neutral CO_2.

Chapter 3. Materials and Methods

3.1 Materials

The materials used in this project were the following: anaerobic biomass, different types of industrial pulp and paper wastewaters, nutrients including potassium hydrogen phosphate and ammonium chloride to support microbial growth and activities, acid and base for pH adjustment, carbon dioxide and nitrogen gas cylinders.

3.1.1 Biomass

Granulated anaerobic biomass was collected from a UASB reactor in the treatment plant of A. Lassonde Inc. (Rougemont, QC, Canada) which produces fruits and vegetable juices. The biomass was kept in an incubator at the experimental temperature (30 and 35^{o}C) for acclimation before use. Figure 3.1 shows the granulated biomass under a laboratory microscope.

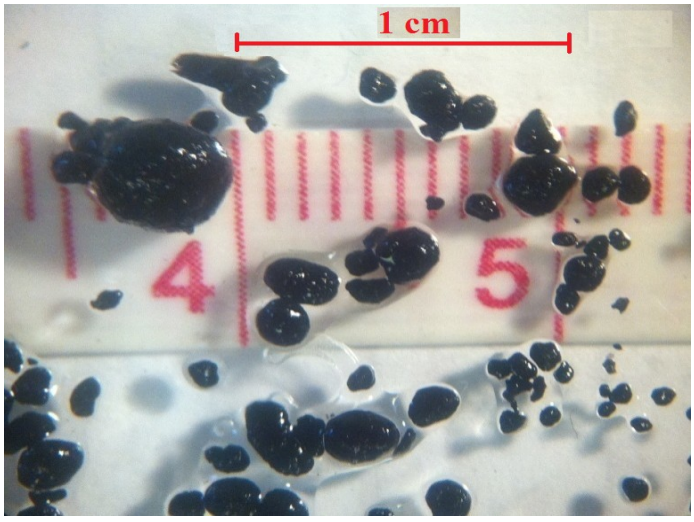


Fig. 3.1: Microscopic image of granular methanogens (50X).

3.1.2 Wastewater as the substrate

The substrates for this project were different types of industrial pulp and paper wastewater, including the following.

- The CTMP wastewater collected from a primary treatment effluent of an anaerobic/aerobic treatment plant at Spruce Falls Inc. (Division Tembec, Matane, QC, Canada). The pH of this wastewater was 5.9 to 6.53 in different streams originating from different activities of the plant.
- The recycled pulp and paper wastewater collected from Cascades Inc. (Kingsey Falls, QC, Canada) which uses recycled papers to produce different paper products such as paper towels. The pH of this wastewater was 5.68 ±0.1.

Elemental analysis of wastewater samples was performed to determine the concentration of nutrients and trace minerals that needed to be added to the wastewater to support the growth of methanogenic bacteria. These analyses showed that the level of heavy metals in the wastewater was less than the toxic limit for methanogens. Table 3.1 presents the elemental analysis of different types of wastewaters used in this project, showing that the wastewaters had all the necessary trace minerals for methanogenic activity and did not require additional supplements. Sources of nitrogen and phosphorus were added to provide a sufficient level of nutrients for bacterial growth (COD: N: P = 200-300: 5: 1) (Xuefei and Nanqi, 2007). Potassium hydrogen phosphate (98%) and ammonium chloride (crystalline 99.5%) used as sources of nitrogen and phosphorus for bacterial growth were provided by Fisher Scientific Ltd. (Montreal, Canada). Solutions of 1 N NaOH and HCl were used to adjust the pH to a desired value between 5.5 and 7.5.

Table 3.1: Analysis of the wastewater

Component[*1]	CTMP[*2] WW	Cascades recycled paper WW	Toxic level for methanogens (The Biogas Technology in China, 1989; Chen et al., 2008)
Sulphate	542.5	>150	5000
Nickel	7.84	1.27	200 - 500
Chlorine	5.52	1.6	
Iron	15.9	5.14	
Aluminum	0.368	0.195	2500
Phosphate	3.32	13.3	
Total nitrogen	22.5	21.3	
COD	9130	2200	
VFA	3580	724	

[*1] All concentrations are in mg/l

[*2] These data belong to the analysis of CTMP wastewater in the second set of samples from the plant

3.1.3 Gases

- A CO_2 gas cylinder with 99% industrial purity purchased from Praxair (Montreal, Canada) was used to saturate the wastewater with carbon dioxide. This purity of CO_2 is not available in the mill environment. However CO_2 with high purity was used to facilitate the study of the feasibility and optimum condition of CO_2 removal. For cost estimation and GHG analysis in the present work the flue emission with a 60% CO_2 concentration was assumed.

- A nitrogen gas cylinder with industrial grade purity was used to purge oxygen from the batch test bottles before starting the test. In order to avoid stripping of dissolved CO_2, only the top of the bottles was purged with nitrogen gas.

In order to avoid high turbulence in the wastewater during gas injection, the gas pressure in the cylinders was reduced by a pressure regulator and the gas was introduced into the liquid by using a fish tank sparger connected to the gas line.

3.2 Methodology

3.2.1 Batch tests

Batch experiments were conducted in 1L glass containers equipped with a rubber septum. The rubber septum enabled sample withdrawal from the bottles without opening their caps and disturbing the anaerobic condition inside the bottles, while preserving the produced biogas in the bottle. 10-ml plastic and 10-ml gas-tight glass syringes were used for liquid and gas sample withdrawal, respectively. The batch tests were performed on CTMP and Cascades wastewaters by filling the bottles with 300 ml wastewater and 25 g VSS/L granulated biomass. For each wastewater, two sets of experiments were carried out, with and without the addition of carbon dioxide. In the experimental set with the addition of CO_2, carbon dioxide was injected into the wastewater until the liquid pH became constant. After pH adjustment to the desired value (from 5.5 to 7.5± 0.10), the bottles were purged with nitrogen gas for 2 minutes and were subsequently placed in incubators at the required temperatures (30 and 35ºC± 3^{o}C). The second set of experiments did not receive any carbon dioxide injection. After pH adjustment and purging with nitrogen gas, the bottles were directly placed inside the incubator. The selection of temperature for these experiments was based on the results of previous work by Abedi et al. (2012) that showed methanogenic activity is much higher at 30 and 35^{o}C compared to 20^{o}C. The produced gases in batch bottles were collected in Tedlar bags and their volumes were measured by water displacement method. Liquid and gas samples were taken several times during the first two days and then once every two days for two weeks. All batch tests were performed at least twice (If the difference between results was more than 10%, more tests were repeated in order to maximize

the precision) and the average results are reported. Figure 3.2 shows the batch phase set up used in this project.

Fig. 3.2: Batch test set up

3.2.2 Continuous operation

The continuous-mode experiments were conducted following the batch operations. These experiments were performed as a one-stage process in which the entire treatment process was carried out in a single reactor (Armfield W8 anaerobic UASB reactor). Two UASB reactors were used in these experiments; one reactor (R_2) was fed with a CO_2-saturated wastewater and another reactor (R_1) was used as a control with no CO_2 injected in its feed. Figure 3.3 shows the experimental set-up used in these experiments.

The working volume of UASB reactors was 5L in which 2L was filled with granular biomass (bacteria) and 3L was filled with the wastewater. The granulated bacteria were acclimated inside the reactor at 35°C for 20 days. The kinetic study of the process used the results obtained during the acclimation period and the batch experiments.

Fig. 3.3: Armfield anaerobic digester W8

After the acclimation of bacteria in the reactor in batch mode, the continuous experiment was started with a very low organic loading rate (OLR=1 g COD/l.d). The OLR was increased gradually and stepwise during the continuous operation to acclimate the biomass. The increase in the organic loading rate was made when the results of COD and VFA removal and methane generation did not change by more than 10% in two successive measurements. The continuous experiment was performed at OLR 1, 2 and 3 g COD/l.d (corresponding to HRT of 6, 3, and 2 days, respectively). Each experiment, at any given OLR, lasted between 5 and 7 hydraulic retention times (HRT) in order to establish process stability and to obtain consistent results. Samples were withdrawn from each reactor at the frequency of three times per week, and were analyzed for COD, VFA, pH, alkalinity, methane content of biogas and the volume of produced gas. Each sample was analyzed at least twice and the average values are reported. At the end of each experiment at any examined OLR, the samples were also analyzed for BOD_5. The temperature was maintained at 35°C based on the results of batch tests which showed a higher efficiency of methane generation at this temperature. In order to be cost effective and to simulate

the real condition in the treatment plant, the continuous experiment was initially performed without the addition of any chemicals to R_1 for pH control. The initial pH of the CTMP wastewater was around 6.5 and it dropped to 5.5 after saturation with CO_2 in R_2. Another continuous experiment was performed, with pH adjustment in the feed of the control reactor (R_1). The pH adjustment in the feed of R_1 was done in order to make the initial pH of both reactors equal and to facilitate the comparison of their outcome. The initial pH in the feed of R_2 after saturation with CO_2 was maintained at 5.5.

The effects of OLR and HRT on the efficiency of CO_2, BOD and COD removal and methane generation were evaluated. As the organic loading rate increased during the one-stage process without pH adjustment, the methane content of produced biogas in the UASB reactor with the CO_2 injection (R_2) decreased which reflected the unfavorable condition in the R_2 reactor. The best pH for methanogenic activity has been reported to be between 6.5 and 7.5 (Lay et al., 1997). The feed to R_2 reactor was saturated with CO_2 and had the pH of 5.5, while the pH of feed to the control UASB reactor was 6.5 (the initial pH of wastewater). Since the pH in R_2 was lower than the optimum pH, the methanogenic activity in this reactor was lower than that in the control reactor. This effect is explained with more details in the next chapter.

3.3 Analytical parameters

3.3.1 Sample withdrawal technique

A 10-ml plastic syringe and a 10 ml gas-tight glass syringe purchased from Fisher Scientific Ltd. (Montreal, Canada) were used for taking the liquid and gas samples, respectively. In batch experiments, liquid and gas samples were withdrawn several times during the first two days and then once every two days for two weeks. In the continuous experiment, samples were taken three times per week. In the batch tests, the time interval between the samples was based on the volume of gas production in bottles (more than 10 ml) and the decrease in the COD concentration (more than 10% reduction).

3.3.2 Volume of biogas

A Tedlar bag, purchased from Fisher Scientific Ltd., connected to a needle was used to collect the produced gas in the experimental bottles. The volume of collected gas in each bag was subsequently measured by the water displacement method (Fig. 3.4). For this purpose, a flask with one inlet and one outlet in the cap was used. The flask was completely filled with a solution of 0.05 N sulfuric acid. The acidified water prevents the dissolution of biogas in water. As the gas in the bag was introduced in the water, water with the same volume as the biogas was displaced from the flask to a graduated cylinder and its volume was measured.

In order to calculate the efficiency of system in terms of methane production, the experimental value of biogas volume can be compared to the theoretical volume of methane production. At standard condition (T= 0ºC and P=1 atm (≈101.3 kPa)) for each gram of COD removed, 0.35 L methane will be produced. The volume of produced methane at other temperature and pH values can be calculated based on Charles and Gay-Lussac's gas law ($P_1V_1/T_1 = P_2V_2/T_2$).

Fig. 3.4: Set up of water displacement method for measuring the volume of biogas

3.3.3 Purity of biogas

The biogas produced during the anaerobic treatment is mainly composed of methane and CO_2 with trace concentrations of other gases. Consequently, the ratio of methane to carbon dioxide demonstrates the composition of produced biogas in each bottle. This ratio was determined by a

gas chromatograph (GC, VARIAN CP 3800 with a TCD detector) using CARBOXEN 1010 PLOT (30mm × 0.53mm) capillary column from SUPELCO with helium as the carrier gas at 225°C inlet temperature, a TCD detector, column oven temperature of 50-100ºC (ramped at 5ºC/min), injection flow of 5 ml/min and run time of 20 min. A standard curve (Appendix A) was made by preparing gas samples with 20, 40, 60, 80, and 90% (vol. /vol.) of methane and recording the associated CH_4/CO_2 ratio. The volume of methane was calculated by multiplying the biogas volume by the methane percentage in the biogas.

3.3.4 Dissolved carbon dioxide concentration in wastewater

The initial and final concentrations of dissolved carbon dioxide in wastewater were calculated by indirect approaches using pH and alkalinity. By knowing the pH and applying equations 3.1 and 3.2, and inserting them in the alkalinity equation (eq. 3.3), the concentration of carbonate is calculated according to bicarbonate concentration (Vanloon and Duffy, 2011).

$$K_w = [H^+][OH^-] \tag{3.1}$$

$$[H^+] = 10^{-pH} \tag{3.2}$$

$$Alkalinity = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] \tag{3.3}$$

The equilibrium between carbonic compounds (eq. 3.4) and the corresponding equilibrium constant were used to calculate the concentration of dissolved carbon dioxide.

$$H_2O + CO_2(aq) \overset{K_1}{\Leftrightarrow} H^+ + HCO_3^- \overset{K2}{\Leftrightarrow} 2H^+ + CO_3^{2-} \tag{3.4}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2(aq)]} = 4.5 \times 10^{-7} M \tag{3.5}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3]} = 4.68 \times 10^{-11} M \tag{3.6}$$

By knowing the concentration of carbonate according to the bicarbonate concentration from equation 3.3 and applying that in equation 3.6, the bicarbonate concentration can be estimated. The bicarbonate concentration in equation 3.5 which shows the equilibrium constant for

conversion of dissolved CO_2 to bicarbonate was then used to estimate the concentration of dissolved carbon dioxide.

The initial and final concentrations of carbonate and bicarbonate in the wastewater can be calculated from the initial and final concentrations of dissolved carbon dioxide by using the constants K_1 and K_2.

In order to determine the concentration of carbon dioxide removed by the conversion process, mass balances for carbon dioxide were used. By knowing the concentration of dissolved carbon dioxide initially [$CO_2(aq)_i$], finally [$CO_2(aq)_f$] and in the biogas [$CO_2(aq)_b$], the removed carbon dioxide [$CO_2(aq)_{rem}$] can be calculated.

$$CO_2(aq)_i - CO_2(aq)_f - CO_2(aq)_b = CO_2(aq)_{rem} \quad (3.7)$$

It should be noted that the removed CO_2 is converted either to methane or to other carbonic compounds (HCO_3^- and CO_3^{2-}). The other method that can be used to measure the concentration of carbon dioxide in the influent is measuring the amount of injected CO_2 using a gas flow meter and the time to reach a constant pH.

3.3.5 Chemical Oxygen Demand (COD)

The elemental analyses of wastewater and COD measurements were done using Hach twist-cap vials purchased from Fisher Scientific Ltd. A Hach UV-VIS spectrophotometer was used to read the absorbance of each sample and to measure its concentration, according to the method approved by the US EPA (2005), as described below:

Principle: The concentration of COD (mg/L) was defined as the concentration of consumed O_2 (mg/L) under the condition of this procedure. In this procedure, the samples were digested with potassium dichromate, a strong oxidizing agent, in the reactor for two hours. The organic compounds in the sample became oxidized and dichromate ion became reduced to green chromic ion. After samples were cooled down to the room temperature, their absorbance was read by a UV-VIS spectrophotometer (Hach procedure manual, 2005).

Interference: Chloride is the primary interference in determining COD concentration. The maximum allowable concentration of chloride in samples for COD measurements is 2000 mg/L (Hach procedure manual, 2005).

3.3.6 Volatile fatty acids (VFAs)

The VFA measurements were done using Hach twist-cap vials from Fisher Scientific Ltd. A Hach UV-VIS spectrophotometer was used to read the absorbance of each sample and show its concentration. The analyzed samples were filtered (pore size of 0.45 µm) to be particle free.

Principle: Volatile fatty acid in the sample reacted with diols in acidic environment to form fatty acid esters. These esters were then reduced by Fe^{3+} salts to form a red complex. The concentration of VFA was measured based on photometric method and the color of the produced complex [Hach procedure manual, 2009].

Interferences: Table 3.2 shows the ions that can interfere with the measurement of VFA in the samples.

Table 3.2: Interference of VFA measurements [Hach procedure manual, 2009]

Interferences	Maximum level allowed (mg/L)
Cl^-, SO_4^{2-}	2000
Na^+,K^+, Ca^{2+}, Mg^{2+}	1000
NH_4^+	250
Al^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, CO_3^{2-}, Cu^{2+}, I^-, Mn^{2+}, Mo^{2+},NO_2^-,Pb^{2+}, S^{2-}, Sn^{2+}, SiO_2, SO_3^{2-}, acetone, acetaldehyde, formaldehyde	50
Zn^{2+}	25
Ni^{2+}	10
Fe^{2+}, Fe^{3+}, Cr^{6+}	5

3.3.7 Total Alkalinity

Alkalinity is the capacity of water to neutralize acids. It is the sum of all titratable bases of water in the form of carbonate, bicarbonate and hydroxide. The standard method No. 2320 was used for the determination of alkalinity in this project which is based on the titration method and the pH of end point in the titration (Clesceri et al., 1998). Bromocresol green was used as the indicator for pH 4.5 which is blue at higher pH values and its color changes to greenish yellow at the end point. The bromcresol green indicator was prepared by dissolving 100 mg dry bromocresol green in 100 ml distilled water. A 0.02 N solution of sulfuric acid was used as a titrant. The volume of acid used for titration in ml was equal to the alkalinity of solution in mg/L

of $CaCO_3$. Equation 3.8 was used for calculation of the alkalinity base on the volume of standard acid that was used for the titration.

$$Alkalinity\ (\frac{mg\ CaCO_3}{L}) = \frac{A \times N \times 50000}{ml\ sample} \tag{3.8}$$

Where,

A= ml acid used for titration

N= normality of standard acid

3.3.8 Microbial parameters (TSS, VSS)

The tests for total suspended solid (TSS) and volatile suspended solids (VSS) were done to measure the biomass concentration in the reactor and also to measure the decrease in the concentration of suspended solids in the effluent in comparison with the influent which is a good method to evaluate the system efficiency. Each test was done at least three times. The tests were carried out according to the following procedure (web 4):

1- Prewash the Gooch crucibles and Whatman binder-free glass microfiber filters GF/A with the pore size of 1.6µm from Fisher scientific Inc. by distilled water before use and dry by vacuum filtration.
2- Put crucibles and filter papers in a 550°C muffle furnace for 15 minutes to dry. (If only the TSS test is desired, the crucibles should be placed in an oven at 105°C for 30 minutes instead of a furnace.)
3- Transfer crucibles and papers into a desiccator to cool and record their weight (Weight A). Handling should be done by forceps.
4- Place the filter on the side-arm Erlenmeyer flask with vacuum gasket. Wet the filter with deionized water. Turn on the vacuum and make sure there is no hole in the papers.
5- Mix the sample, and transfer a specific volume of sample to the filter on a vacuum filter and rinse the filter with 10 ml deionized water (the residue on the filter should be between 2.5 to 200 mg).

6- Place the crucibles and filters in the oven at 105°C to dry for at least 1 hour. Transfer the dried filters to a desiccator to cool and then weigh it and record the weight (weight B).
7- Place the crucibles and filters for 30 minutes into a 550°C furnace and then allow the samples to cool down in a desiccator and record the weight (weight C).
8- Equations 3.9 and 3.10 are applied to determine the concentration of TSS and VSS.

$$Total\ suspended\ solids\ (\frac{mg}{L}) = \frac{(B-A)\times 1000}{sample\ volume\ (ml)} \tag{3.9}$$

$$Volatile\ suspended\ solids\ (\frac{mg}{L}) = \frac{(B-C)\times 1000}{sample\ volume\ (ml)} \tag{3.10}$$

3.3.9 Hydraulic retention time (HRT)

The hydraulic retention time (HRT) or hydraulic residence time in each reactor is the average time that wastewater remains in that reactor and was calculated based on the equation 3.11.

$$HRT\ (d) = \frac{Volume\ of\ tank\ (m^3)}{Design\ flow\ (m^3/d)} \tag{3.11}$$

3.3.10 Organic loading rate (OLR)

The organic loading rate was calculated based on the design flow, the concentration of organic matters in the wastewater and the volume of the reactor as shown in the equation 3.12.

$$Organic\ loading\ rate = \frac{organic\ matter\ (\frac{g\ BOD_5}{m^3}) \times design\ flow\ (\frac{m^3}{d})}{volume\ (m^3)} \tag{3.12}$$

3.3.11 Biogas rate

The biogas production rate during the continuous operation was calculated by connecting the reactor gas exit to a U-shape tube that was partially filled with acidified water and measuring the displacement of water in the this tube (Δh) over the duration of displacement, as shown in equation 3.13.

$$\text{Biogas production rate} = \Delta h/t \tag{3.13}$$

3.3.12 Methanogenic activity

Methanogenic activity or the specific methanogenic activity (MA or SMA) is the substrate-dependent rate of methane production per unit mass of volatile solids biomass. The rate of methane production is equal to the slope of the diagram of cumulative methane production over time as is shown in Figure 3.5 (Sørensen and Ahring, 1993).

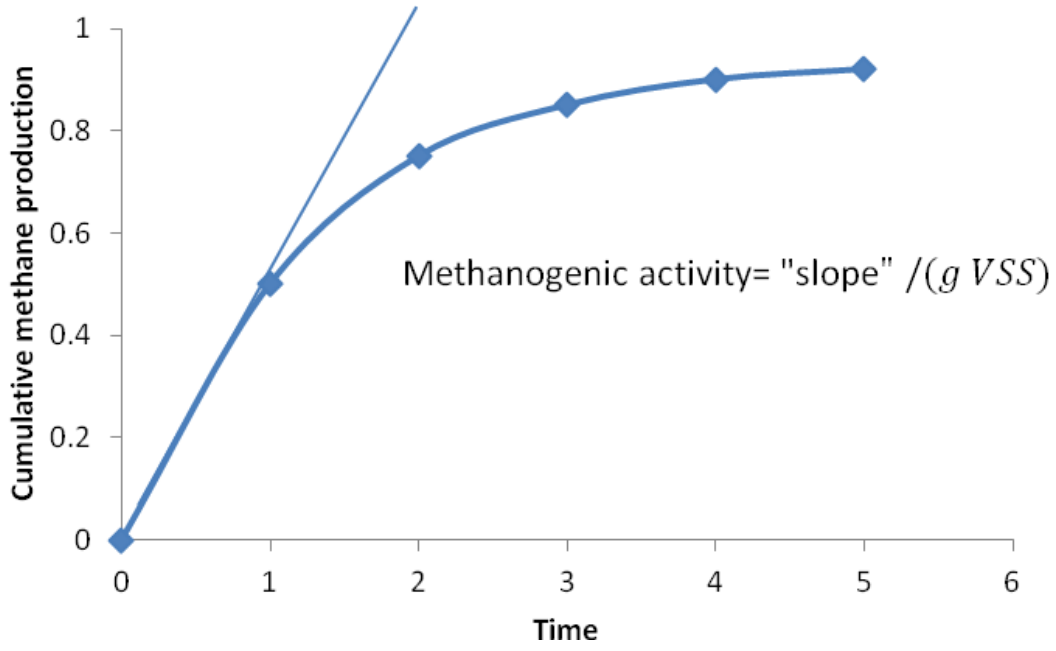


Fig. 3.5: Methanogenic activity

3.3.13 System efficiency

The system efficiency was evaluated based on the following parameters: methane production per amount of COD consumed followed by comparison with the theoretical value (0.35 L methane/gram of COD removed under standard conditions), and the efficiency of CO_2 and COD removal as shown in equations 3.14 and 3.15 in which $COD_i, COD_f, CO_2(aq)_i, CO_2(aq)_e, and\ CO_2(aq)_b$, represent the concentrations of initial COD, final COD, initial dissolved CO_2, converted CO_2, and CO_2 in the biogas, respectively.

$$CO_2\ removal\ \% = \frac{(CO_2)_{rem}}{CO_2(aq)_i} = \frac{CO_2(aq)_i - CO_2(aq)_e - CO_2(aq)_b}{CO_2(aq)_i} \times 100 \quad (3.14)$$

$$COD\ removal\ \% = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (3.15)$$

3.4 Kinetic Study of the System

The numerical values of kinetic parameters, particularly the specific growth rate (μ) and half-saturation constant (K_s) were estimated by conducting a kinetic study of the examined process, using the Monod equation and its derivatives (equations 3.16-3.18). The initial values of parameters were obtained from the literature [ADM1, 2004; Alimahmoodi, 2009]. A statistical procedure based on the Runge-Kutta fourth-order method was used to minimize the difference between the experimental data and model predictions (Press et al., 1992). The Excel 2010 solver program was used in this study.

$$\mu = \frac{\mu_m S}{K_S + S} \quad (3.16)$$

$$\frac{dX}{dt} = \frac{\mu_m SX}{K_S + S} - k_d X \quad (3.17)$$

$$\frac{dS}{dt} = \frac{-1}{Y}\frac{dX}{dt} \quad (3.18)$$

Where

X= microbial concentration in the bioreactor (g/L)

S= substrate concentration (g/L)

μ_m = maximum growth rate of biomass (1/d),

K_s = half-saturation constant (g/L or mM),

k_d= biomass decay rate (1/d),

Y= microbial yield coefficient (microbial mass/ mass of substrate consumed)

Two sets of data were used in the kinetic study: first set of data were obtained from the batch experiments in a 1-L container using the Cascades recycled paper wastewater, and the second set was obtained from the 5-L reactor operation in batch mode using the CTMP wastewater. Based on the estimated values of kinetic parameters, the experimental values of COD concentration at different operating conditions were compared to the corresponding simulated values.

Before starting the continuous operation, in order to measure the kinetic parameters and to acclimate the bacteria, 5-L UASB reactors were initially filled with 25 g VSS/L and the CTMP wastewater. At this stage, both reactors were working in batch mode for two weeks under identical operating conditions at 35°C with the same amount of biomass and wastewater. No chemicals were added to control the pH inside the reactors and the pH was maintained at approximately 7.2 inside the reactors. The COD concentration was monitored during the three week batch operation of the experimental system and the estimated kinetic parameters were compared to those obtained during the batch operation on recycled paper wastewater in the 1-L container.

Chapter 4: Results and Discussion

In this chapter, the effect of operating conditions (temperatures of 30 and 35ºC and pH 5.5-7.5) and the presence or absence of carbon dioxide injection on the efficiencies of CO_2 and COD removal and methane generation in the batch tests using the CTMP and Cascades recycled paper wastewaters are presented. The selection of temperature for these experiments was based on the results of previous work by Abedi et al. (2012) that showed that methanogenic activity is higher at 30 and 35ºC compared to 20ºC.

Following the batch tests, the results of continuous experiments on CTMP wastewater are reported and the effect of different OLR and HRT on the efficiencies of CO_2 and COD removal and methane generation were evaluated. In the figures of this chapter, the difference between the average and maximum/minimum values are shown as error bars. In all experiments, the results obtained with samples having CO_2 injection were compared with those obtained with control samples without CO_2 injection to improve the accuracy of reported results.

4.1 Batch Experiments

4.1.1 Carbon dioxide removal

The fate of carbon dioxide was studied by applying mass balances for CO_2 and by calculating CO_2 participation in different pathways. The implicated pathways include the removal of CO_2 by bioconversion into methane or other compounds, conversion to other carbonic compounds (HCO_3^- and CO_3^{2-}) and emission in the biogas. A fraction of CO_2 will remain dissolved in the solution (Figs. 4.1 to 4.4).

Equations 3.1 to 3.6 were used to calculate the initial and final concentrations of all carbonic compounds (CO_2, HCO_3^-, and CO_3^{2-}) and changes in their respective concentrations. Mass balances for carbon dioxide along with the calculation of concentrations of different types of

CO_2 in solution were used to estimate the amount of CO_2 that participated in different pathways. The estimated carbon dioxide participation in different pathways at different pH values in the presence and absence of added CO_2 are presented in Fig.4.1 and 4.2 for Cascades wastewater and Fig.4.3 and 4.4 for CTMP wastewater. The results show that at all pH values examined in the present work, CO_2 removal by bioconversion into methane is higher in samples with CO_2 injection compared to the control samples with no CO_2 injection. For example for Cascades wastewater, at pH 5.5 and 35°C the CO_2 removal by bioconversion into methane in samples with CO_2 injection is 515 mg/l (29%) higher than the control sample. The corresponding value at pH 7.5 equals to 13 mg/l (19%) higher than the control sample. These results show the feasibility of CO_2 removal through the anaerobic treatment of wastewater. Results also show that CO_2 removal is higher at lower pH values. For example, at pH 7.5 and 35°C the CO_2 removal by bioconversion into methane in samples with CO_2 injection is 81 mg/l, while this value at pH 5.5 is 2240 mg/l. It should be noted that due to higher methanogenic activities at higher pH values compared to those at the pH 5.5-6, the absolute percentage of CO_2 removal, estimated as (CO_2 participated in removal pathway/total dissolved CO_2) is higher at higher pH values. For example for Cascades wastewater, samples with CO_2 injection at 35°C showed 64 and 72% CO_2 removal at pH 5.5 and 7.5, respectively. However, the initial concentration of dissolved CO_2 at higher pH values are much lower than that at lower pH values, which results in lower amounts of CO_2 removal. For example, the 64 and 72% CO_2 removal at pH 5.5 and 7.5, respectively, correspond to 2240 and 81 mg/l CO_2 removal. At lower pH values, the concentration of dissolved carbon dioxide (in the form of carbonic acid) is higher. By increasing the pH, the equilibrium between carbonic compounds (eq. 3.4) shifts toward the production of H^+, according to Le Chatelier's principle. Therefore, the equilibrium shifts from the dissolved carbon dioxide toward bicarbonate and carbonate compounds. Consequently, the concentration of CO_2 (aq) which serves as the substrate for methanogenic bacteria decreases. Therefore, less CO_2 will be available to participate in the conversion to methane.

The effect of temperature on the initial concentration of dissolved CO_2 and CO_2 removal efficiency can be explained by comparing Figures 4.1 and 4.2 for the Cascades wastewater or Figures 4.3 and 4.4 for the CTMP wastewater which show that at 30°C the initial concentaration of dissolved CO_2 was higher than that at 35°C. Also, the results for both wastewaters demonstrate that at 35°C and at all pH values, the increse in CO_2 removal by bioconversion to

methane in samples with CO_2 injection compared to the control samples with no CO_2 injection was 3-6% higher than that obtained at 30°C. This can be explained by the higher methanogenic activity at 35°C compared to 30°C which increases the conversion of CO_2 to methane.

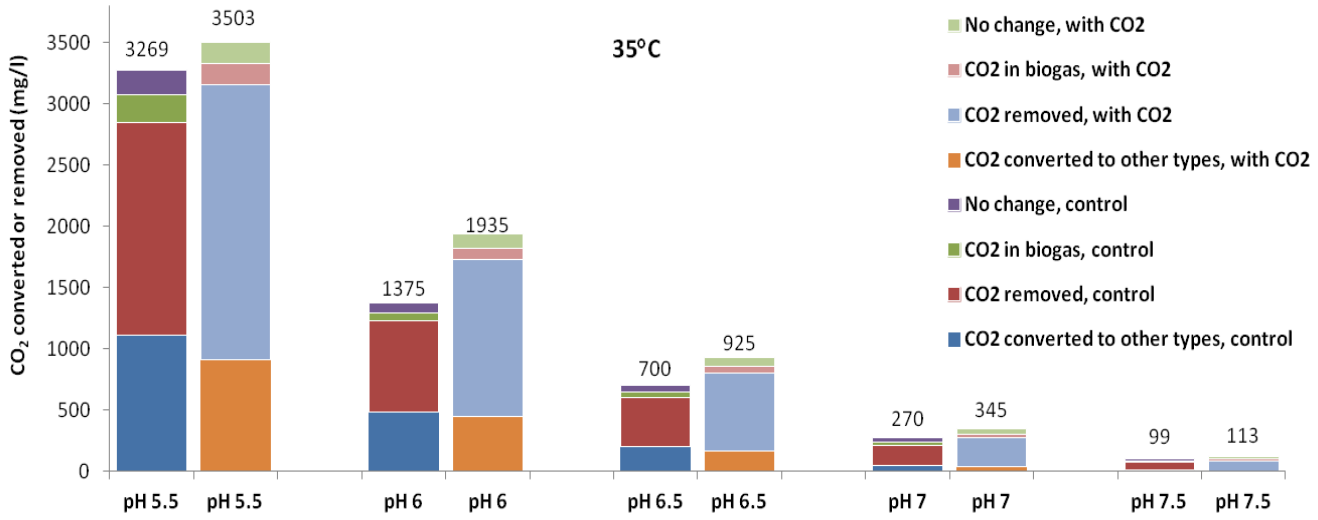


Fig. 4.1. CO_2 removal at 35°C and various pH values and in the presence and absence of added CO_2 for Cascades wastewater. The initial concentration of dissolved carbon dioxide is shown on top of each bar. At each pH, the bar on the left is related to the control samples without CO_2 injection and the bar on the right is for the sample with CO_2 injection.

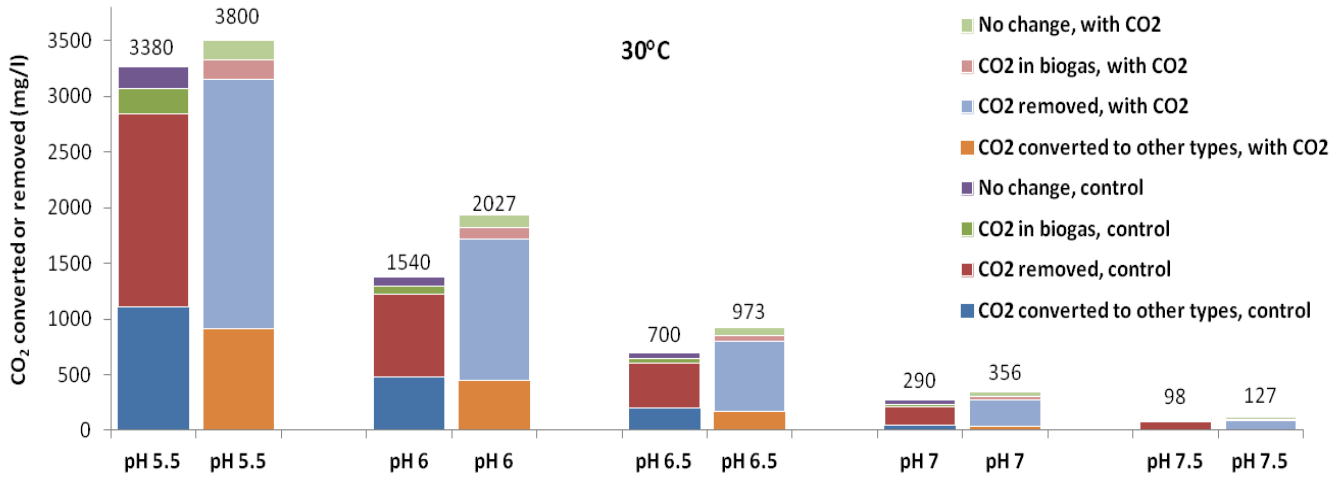


Fig. 4.2. CO_2 removal at 30°C and various pH values and in the presence and absence of CO_2 for Cascades wastewater. The initial concentration of dissolved carbon dioxide is shown on top of each bar. At each pH, the bar on the left is related to the control samples without CO_2 injection and the bar on the right is for the sample with CO_2 injection.

The fate of carbon dioxide in CTMP wastewater is shown in Figures 4.3 and 4.4. It can be seen that at all pH values, the initial concentration of dissolved CO_2 in CTMP wastewater is higher than the concentration in Cascades wastewater. This is because of higher alkalinity and buffering capacity of CTMP wastewater (approximately twice as much) compared to the Cascades wastewater which results in a higher capacity for CO_2 dissolution.

The results of CO_2 removal for CTMP wastewater also show that at all pH values examined in the present work, CO_2 removal by bioconversion into methane is higher in samples with CO_2 injection compared to the control samples with no CO_2 injection. For example, at pH 5.5 and 35°C the CO_2 removal by bioconversion into methane in samples with CO_2 injection is 1440 mg/l (45%) higher than the control sample. The corresponding value at pH 7.5 equals to 40 mg/l (38%) higher than the control sample. Results also show that CO_2 removal is higher at lower pH values. For example at pH 7.5 and 35°C the CO_2 removal by bioconversion into methane in samples with CO_2 injection is 150 mg/l, while this value at pH 5.5 is 4650 mg/l. In this wastewater, similar to Cascades wastewater, due to higher methanogenic activities at higher pH values compared to those at pH 5.5-6, the absolute percentage of CO_2 removal is higher at higher pH values. For example samples with CO_2 injection at 35°C, showed 59 and 72% CO_2 removal at pH 5.5 and 7.5 respectively. However, the initial concentration of dissolved CO_2 at higher pH values are much lower than lower pH values, which results in lower values of CO_2 removal. For example, the 59 and 72% CO_2 removal at pH 5.5 and 7.5 respectively corresponds to 4650 and 150 mg/l CO_2 removal.

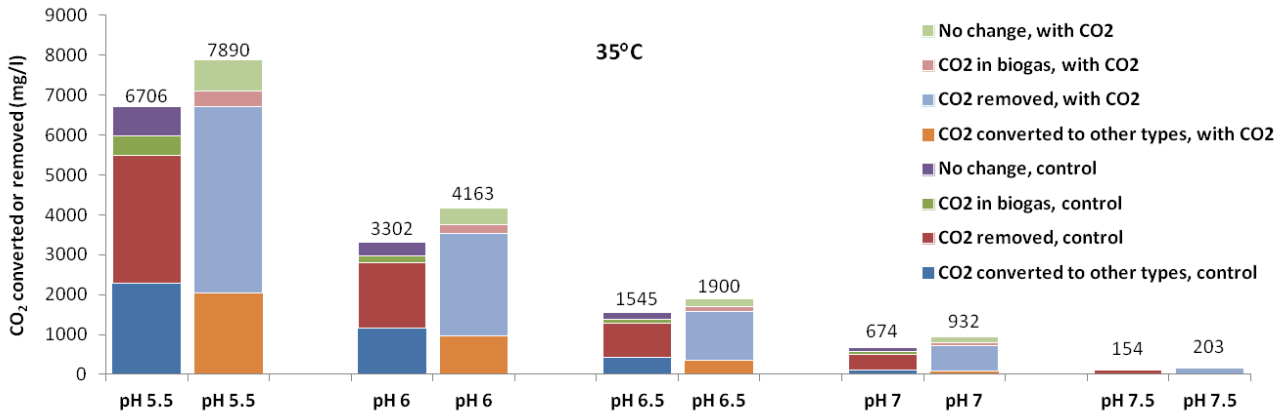


Fig. 4.3. CO_2 removal at 35°C and various pH values and in the presence and absence of added CO_2 for the CTMP wastewater. The initial concentration of dissolved carbon dioxide is shown on top of each bar. At each pH, the bar on the left is related to the control samples without CO_2 injection and the bar on the right is for the sample with CO_2 injection.

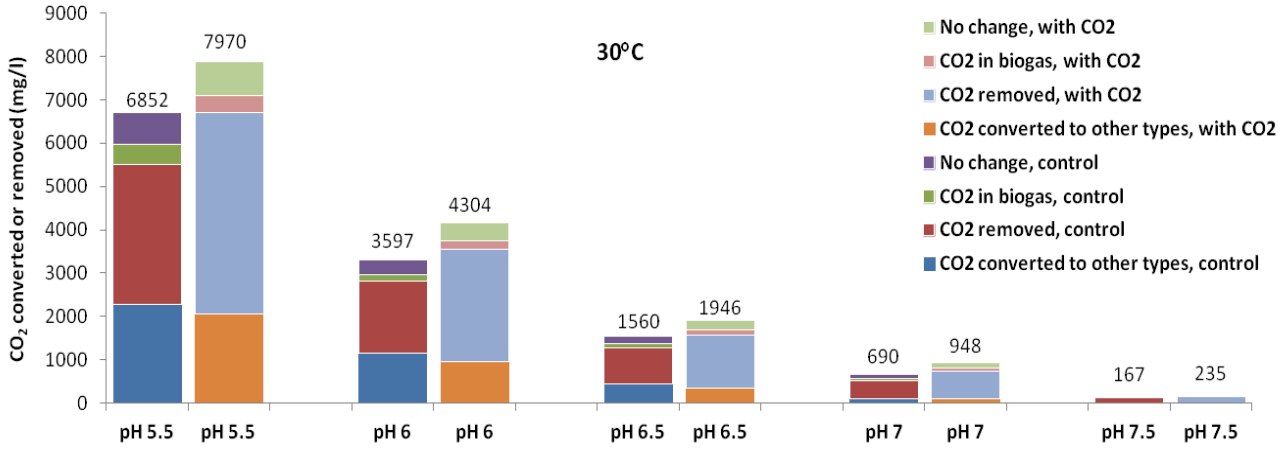


Fig. 4.4. CO_2 removal at 30°C and various pH values and in the presence and absence of CO_2 for the CTMP wastewater. The initial concentration of dissolved carbon dioxide is shown on top of each bar. At each pH, the bar on the left is related to the control samples without CO_2 injection and the bar on the right is for the sample with CO_2 injection.

4.1.2 COD removal efficiency

The result of COD removal efficiency for CTMP wastewater at different operating conditions is summarized in Figure 4.5. The effect of operating pH, temperature, and injection of carbon

dioxide on the COD removal efficiency was investigated. The results illustrate that all samples showed similar efficiencies for COD removal under different conditions after two weeks of the batch test.

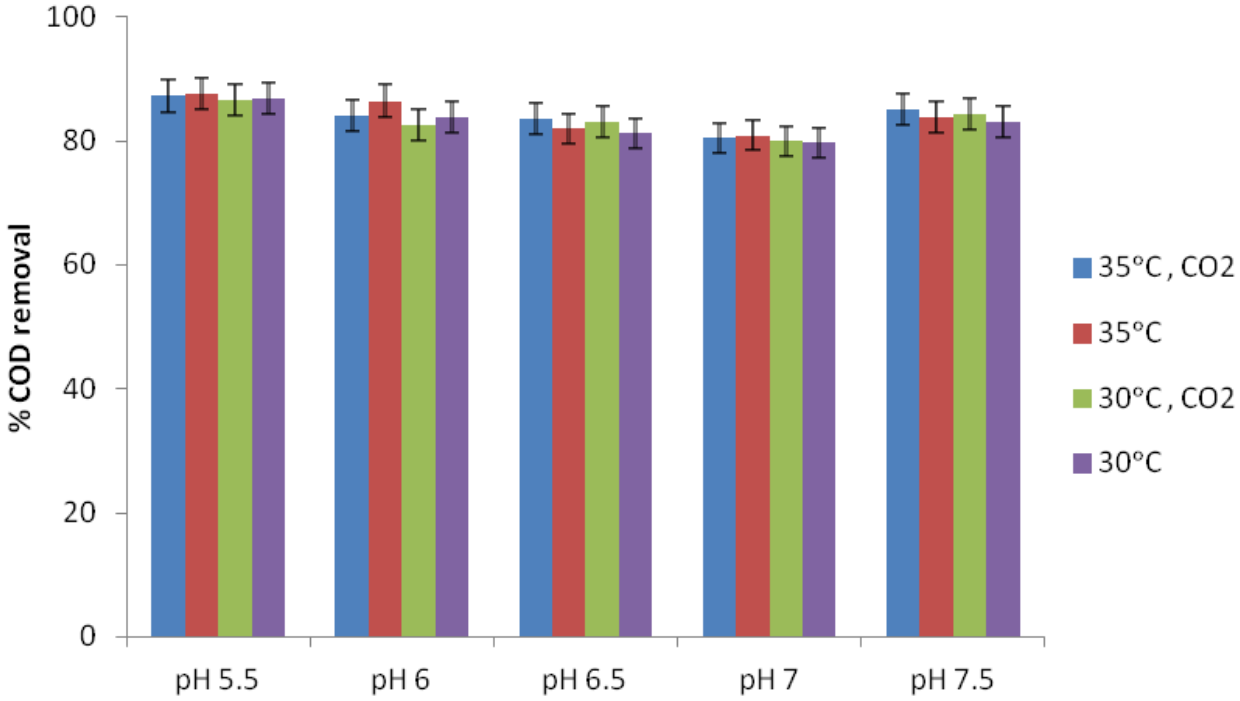


Fig. 4.5: COD removal efficiency of the CTMP wastewater at different temperatures and pH values, in the presence or absence of CO_2

Figure 4.6 shows the COD removal for recycled paper wastewater at different operating conditions. The results show that for recycled paper wastewater, like the CTMP wastewater, COD removal is almost the same at different temperatures and pH values and in the absence or presence of CO_2 injection. The COD removal efficiency for both wastewaters was 84±4%. It is important that the injection of CO_2 into the wastewater does not have any detrimental effect on wastewater treatment and COD removal.

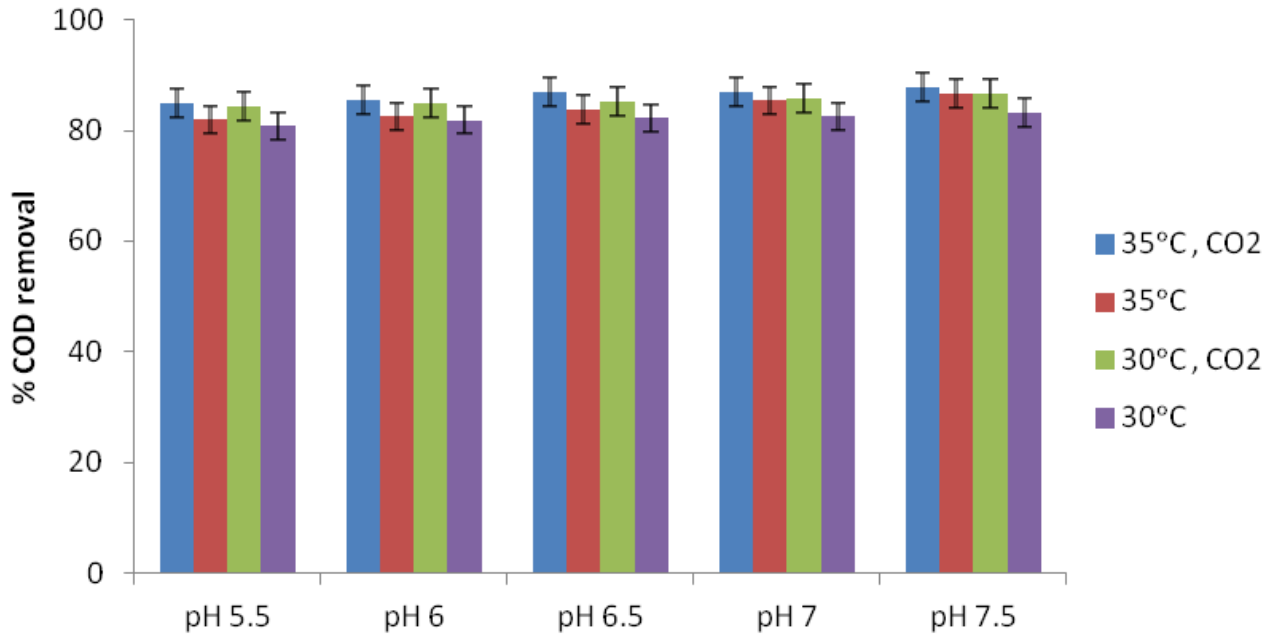


Fig. 4.6: COD removal efficiency of the recycled paper wastewater at different temperatures and pH values, in the presence or absence of CO_2

4.1.3 COD removal rate

4.1.3.1 Effect of pH on COD removal rate

For the CTMP wastewater, the COD removal was mostly completed in the first two days. To evaluate the effect of pH on COD removal rate, temperature was kept constant and the rate of COD removal at different pH values was calculated. The COD removal rate at different pH values and at a constant temperature is shown in Figures 4.7 and 4.8. It can be observed that the rate of COD removal increased during the first hours of test and reached its maximum after three hours, followed by a smooth decrease. After the first days of operation, the rate of COD removal was very low and stayed almost constant. It was shown that COD reduction rates were almost similar at different pH values.

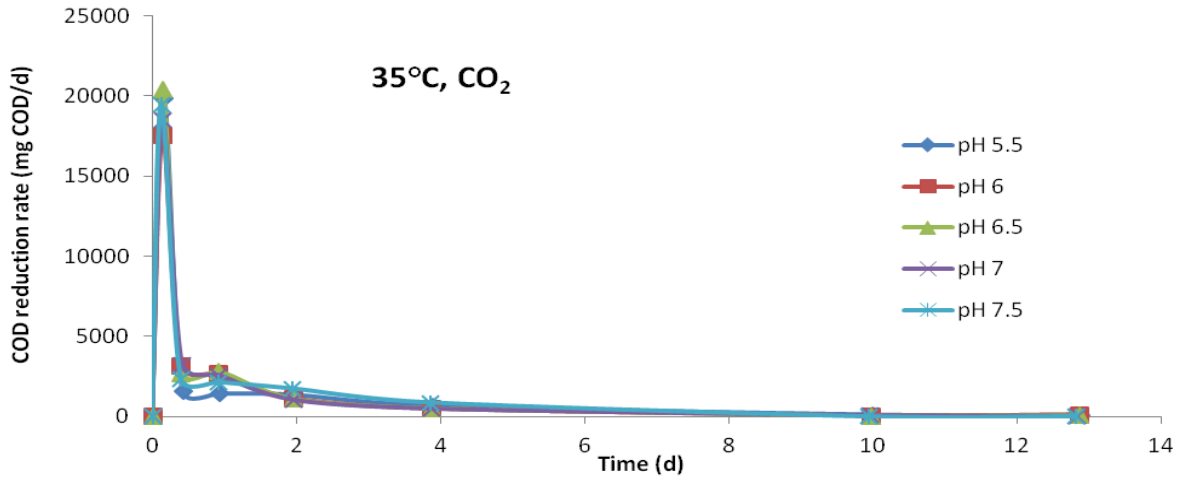


Fig. 4.7: Effect of pH on COD reduction rate with the CTMP wastewater at 35°C, with CO_2 injection

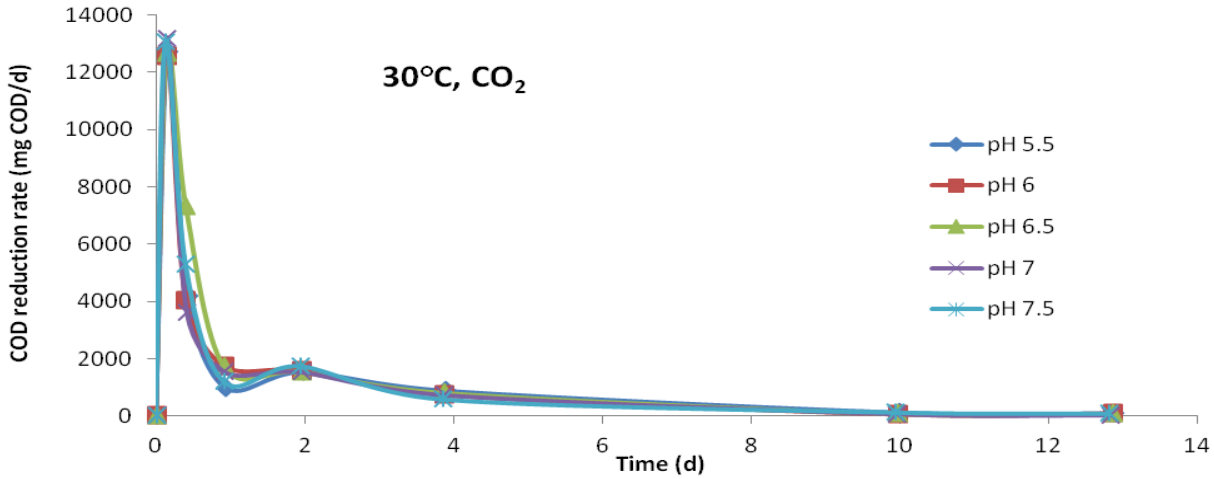


Fig. 4.8: Effect of pH on COD reduction rate with the CTMP wastewater at 30°C, with CO_2 injection

In order to show the effect of pH on COD removal for the recycled paper wastewater, the rate of COD removal at a constant temperature with CO_2 injection is shown in Figures 4.9 and 4.10. As shown in these figures, at constant temperature and at all examined pH values, COD reduction follows the same trend. The results show that similar to the trends observed with the CTMP wastewater, COD reduction rate increased in the first hours of experiment and reached its maximum after 3 hours from the beginning of test and then it decreased. Unlike the CTMP wastewater, in the recycled pulp and paper wastewater, the COD reduction was almost negligible after the first day of experiment. This was because of the lower initial COD of recycled paper

wastewater (2200 mg/l) compared to the CTMP wastewater (9100 mg/l) which was consumed by bacteria in a shorter time. In each temperature, the rate of COD reduction for recycled paper wastewater were almost similar at different pH values. For example, at different pH values, the COD reduction rate in samples with the injection of CO_2 at 35°C was 12000±400 mg COD/d, and at 30°C was 7700±400 mg COD/d.

The comparison of COD reduction rate in CTMP and recycled paper wastewater at different pH values shows that the maximum reduction rate was higher in the CTMP wastewater. For example, the maximum reduction rates for the CTMP wastewater at 35 and 30°C were approximately 20000±100 and 13000±100 mg COD/d, respectively, while these values for the Cascades wastewater were approximately 12300±100 and 8100±100 mg COD/d, respectively. This is related to the higher initial COD of the CTMP wastewater which provided bacteria with more substrate compared to the Cascades wastewater.

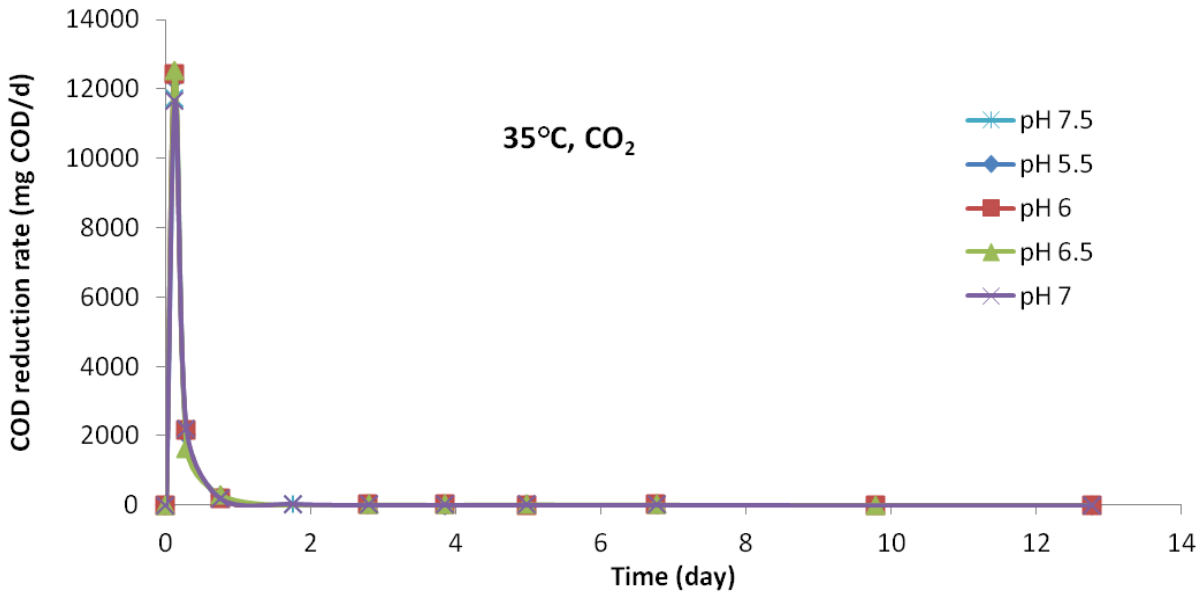


Fig. 4.9: Effect of pH on COD reduction rate for the recycled paper wastewater at 35°C, with CO_2 injection

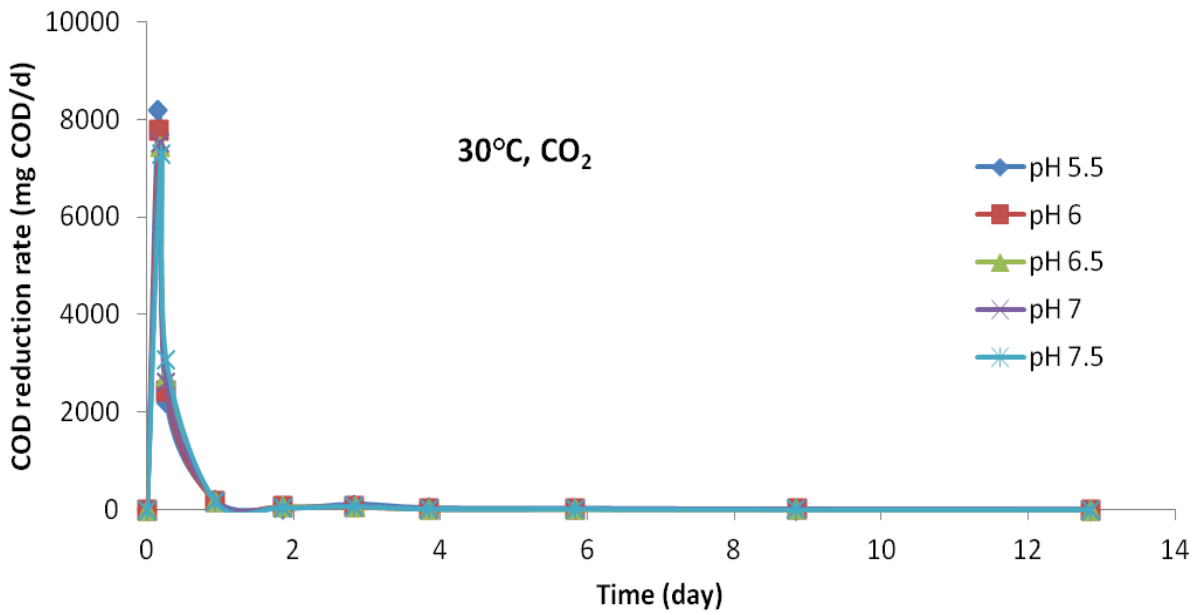


Fig. 4.10: Effect of pH on COD reduction rate for the recycled paper wastewater at 30°C, with CO_2 injection

4.1.3.2 Effect of temperature and CO_2 injection on COD removal rate

To evaluate the effect of temperature and carbon dioxide injection on COD removal rate in the CTMP and recycled paper wastewaters, the liquid pH remained constant and the COD reduction rate at different temperatures in the presence and absence of CO_2 injection was plotted. The effect of each parameter (temperature or carbon dioxide injection) is evaluated while the other parameter remained constant (Figs. 4.11 and 4.12).

The results for the CTMP and Cascades wastewater (Fig. 4.11 and 4.12) demonstrate that CO_2 injection didn't show a significant effect on the COD removal rate, while temperature highly affect it. At a constant pH, when the temperature was higher, the COD reduction rate was higher. From Figure 4.11 it can be seen that for the CTMP wastewater at pH 5.5 and 35°C, the maximum COD reduction rate in samples with and without carbon dioxide injection was 19890±100 and 19325±100 mg COD/d, respectively, which can be compared to the values obtained at 30°C which were 12700±100 and 10890±100 mg COD/d, respectively. From Figure 4.12 it can be seen that for the Cascades wastewater at pH 5.5 and 35°C, the maximum COD reduction rate in samples with and without carbon dioxide injection was 12275±100 and 11610±100 mg COD/d,

respectively, which are higher than the values obtained at 30°C which were 8180±100 and 8000±100 mg COD/d, respectively.

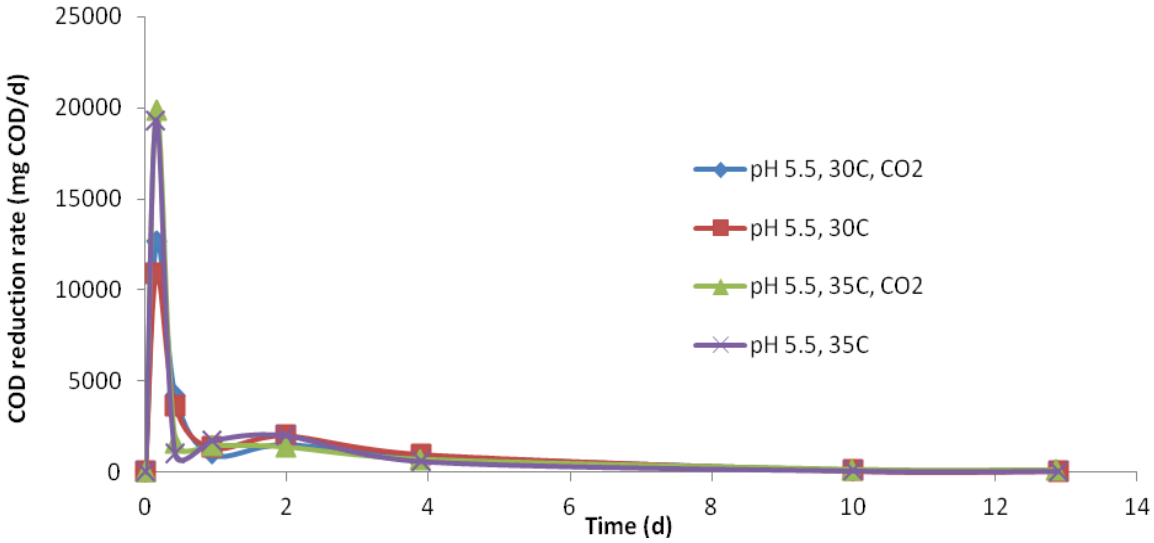


Fig. 4.11: Effect of temperature and CO_2 injection on COD reduction rate with the CTMP wastewater at pH 5.5

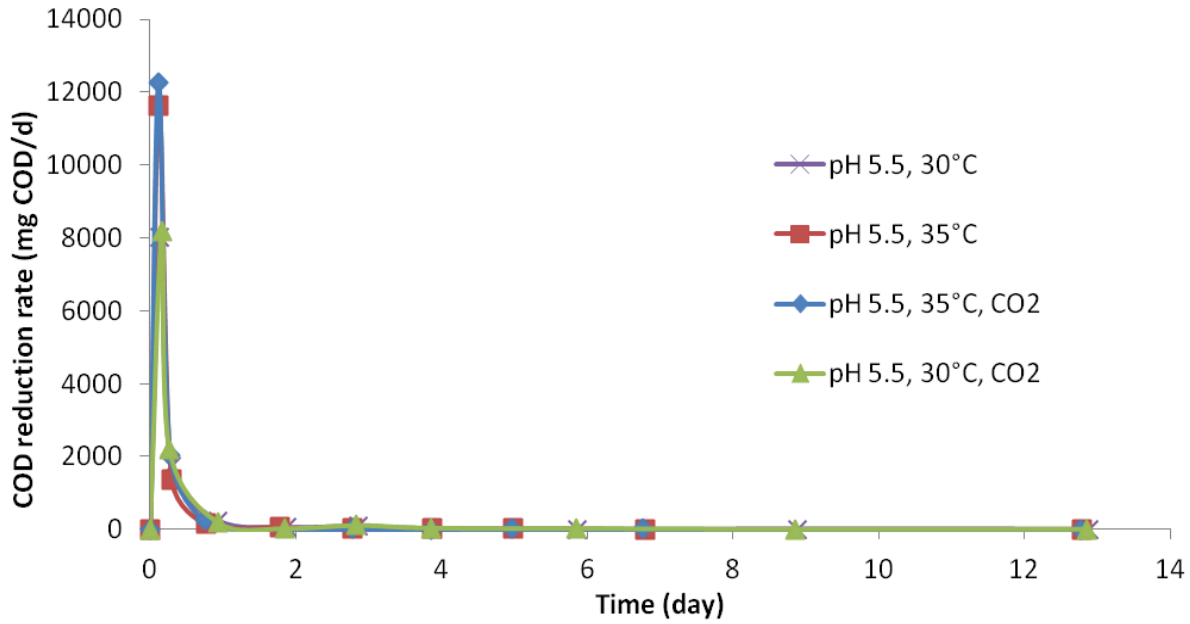


Fig. 4.12: Effect of temperature and CO_2 injection on COD reduction rate with the recycled paper wastewater at pH 5.5

4.1.4 Methane production

Methane generation in the CTMP wastewater started after several hours from the beginning of the batch test and continued throughout the process. The purity of produced methane was very low during the first few hours (approximately 0-73% with the average of less than 10%) and gradually increased in the first day (almost 30-85% with the average of 48% at the end of the first day). Methane purity increased during the batch test and at the end of experiment it was 60-85% with an average of 70%.

Methane generation in the recycled paper wastewater started from the first hour of the experiment and its initial purity (approximately 30-75% with the average of 45%) was higher than that in the CTMP wastewater. The purity of produced methane in this wastewater increased during the first day, reaching approximately 50±10%, and remained almost constant during the experiment.

4.1.4.1 Effect of CO_2 injection on methane production

In order to evaluate the effect of different operating conditions on methane generation, in each case all parameters except the target parameter were kept constant. For example, in order to follow the effect of CO_2 injection on methane generation, temperature and pH were kept constant. Figures 4.13 and 4.14 show the effect of CO_2 injection on methane generation with the CTMP wastewater at 35 ºC and 30 ºC, respectively.

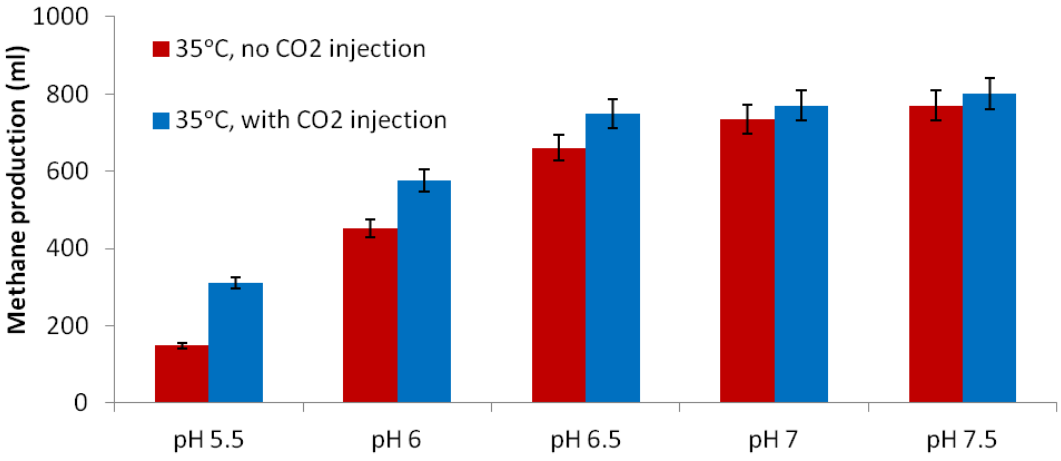


Fig. 4.13: Effect of CO_2 injection on methane generation at a constant temperature (35ºC) with the CTMP wastewater

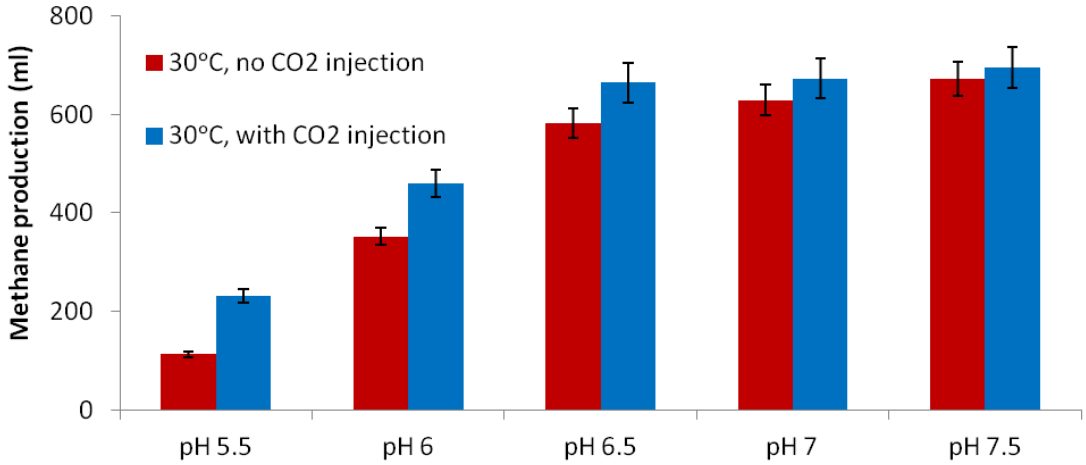


Fig. 4.14: Effect of CO_2 injection on methane generation at a constant temperature (30°C) with CTMP wastewater

From Figs. 4.13 and 4.14, it can be observed that increased methane generation corresponds to higher pH values, and at pH 7.5 and pH 7 more methane was produced compared to the results at pH 5.5 and 6. These observations are compatible with the literature-cited reports that showed the methanogenic activity is higher over the pH range of 6.6–7.8 with an optimum pH of 6.8 (Lay et al., 1997). Also, it can be concluded that for the CTMP wastewater at all experimental conditions (different pH and temperatures), carbon dioxide injection into the wastewater increased methane generation. The increase in methane generation in samples with CO_2 injection compared to the control samples without CO_2 injection was higher at lower pH values. This can be explained based on the fact that at lower pH values more CO_2 was dissolved in the wastewater which was later converted into methane. On the other hand, although at higher pH values methane generation is higher than that at lower pH values, the increase in methane generation by the injection of CO_2 to the wastewater is lower. The reason for this observation is that at higher pH of 7 and 7.5 only a small amount of CO_2 was dissolved in the wastewater and was later converted to methane. Therefore, at higher pH values, the difference in methane generation in the presence and absence of CO_2 injection was less than that observed at lower pH values. For example, at 35°C in the absence of CO_2 injection, methane generation at pH 5.5 and 7.5 was 149 and 770 ml, respectively. The injection of CO_2 into the wastewater increased methane generation by 162 ml (108%) at pH 5.5 and by 22 ml (3%) at pH 7.5.

Figures 4.15 and 4.16 present the effect of CO_2 injection on methane generation in the recycled paper wastewater at 35 and 30ºC, respectively. The results of methane generation in the recycled paper experiment showed the same trend as the CTMP wastewater. For example, at 35ºC in the absence of CO_2 injection, methane generation at pH 5.5 and 7.5 was 58 and 220 ml, respectively. The injection of CO_2 into the wastewater increased methane generation by 54 ml (93%) at pH 5.5 and by 8 ml (4%) at pH 7.5. At all operating conditions (pH and temperatures), the cumulative methane generation in the CTMP wastewater (110-790 ml) was higher than the observed values in the Cascades wastewater (40-230 ml). This was related to the higher COD of CTMP wastewater (9100 mg/l) compared to the recycled wastewater (2200 mg/l).

The fact that methane production was higher in samples with the injection of carbon dioxide is an outstanding result that can be attributed to the bioconversion of carbon dioxide to methane. In these samples, CO_2 was used as a substrate for methanogenesis which is the last step of anaerobic digestion process.

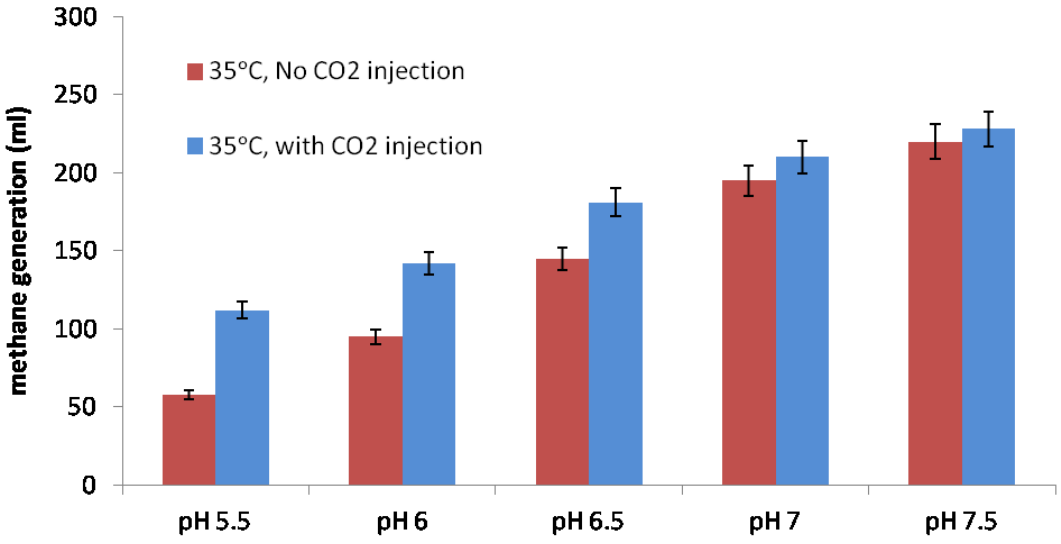


Fig. 4.15: Effect of CO_2 injection on methane generation at a constant temperature (35ºC) with the recycled paper wastewater

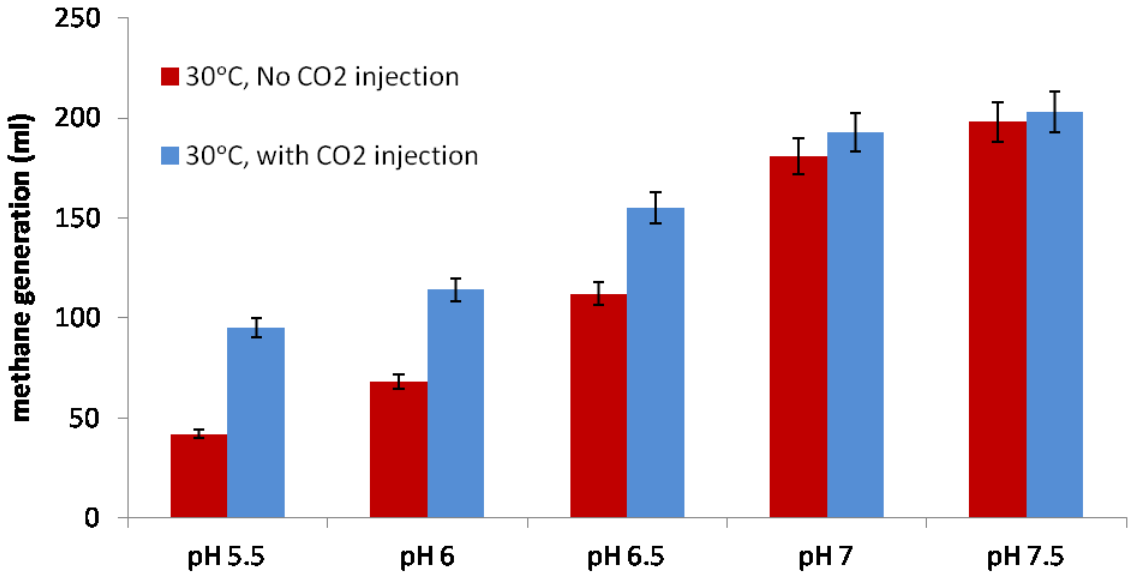


Fig. 4.16: Effect of CO_2 injection on methane generation at a constant temperature (30ºC) with the recycled paper wastewater

The reported methane generation for CTMP and recycled paper wastewater was for the batch test using 300 ml wastewater and 25 g VSS/l of biomass, which is equal to 4.4-31.6 ml methane production / g VSS of biomass for the CTMP wastewater and 1.6-9.2 ml methane production / g VSS for the recycled paper wastewater. As mentioned earlier, the higher methane generation in the CTMP wastewater was the result of higher COD of this wastewater.

4.1.4.2 Effect of temperature on methane production

The effect of temperature on methane production in the CTMP wastewater is presented in Figures 4.17 and 4.18. It can be observed that at any given pH in the sample with carbon dioxide injection (Fig. 4.17) or without carbon dioxide injection (Fig. 4.18), more methane was generated at the higher examined temperature. For example, at pH 5.5-7.5 and in the presence of CO_2 injection methane generation was 80-97 ml (14-35%) higher at 35ºC compared to the volume produced at 30ºC. This observation was compatible with the reports from the literature that shows higher methanogenic activity at 35ºC compared to 30ºC (Kim et al., 2006).

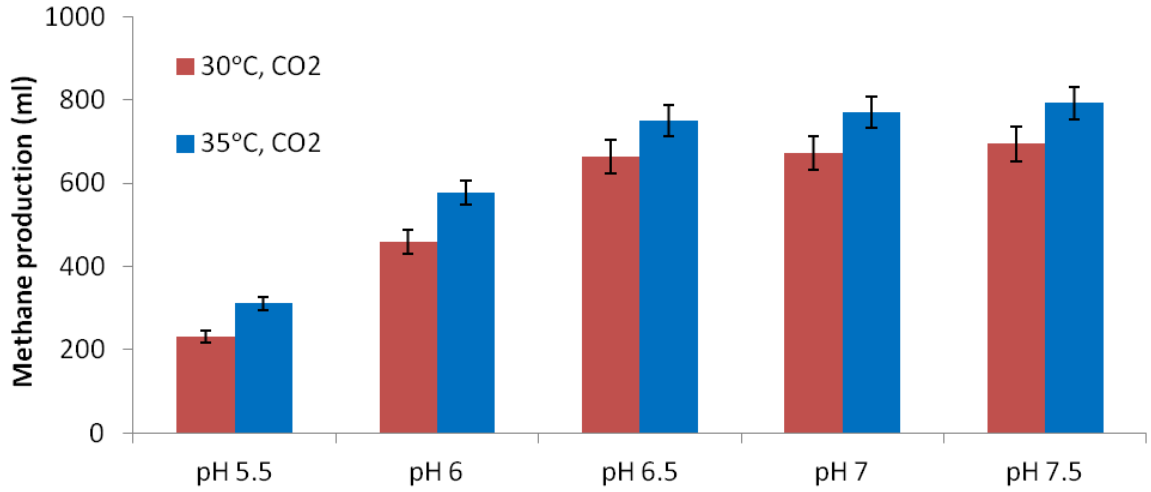


Fig. 4.17: Effect of temperature on methane generation in samples with CO_2 injection with the CTMP wastewater

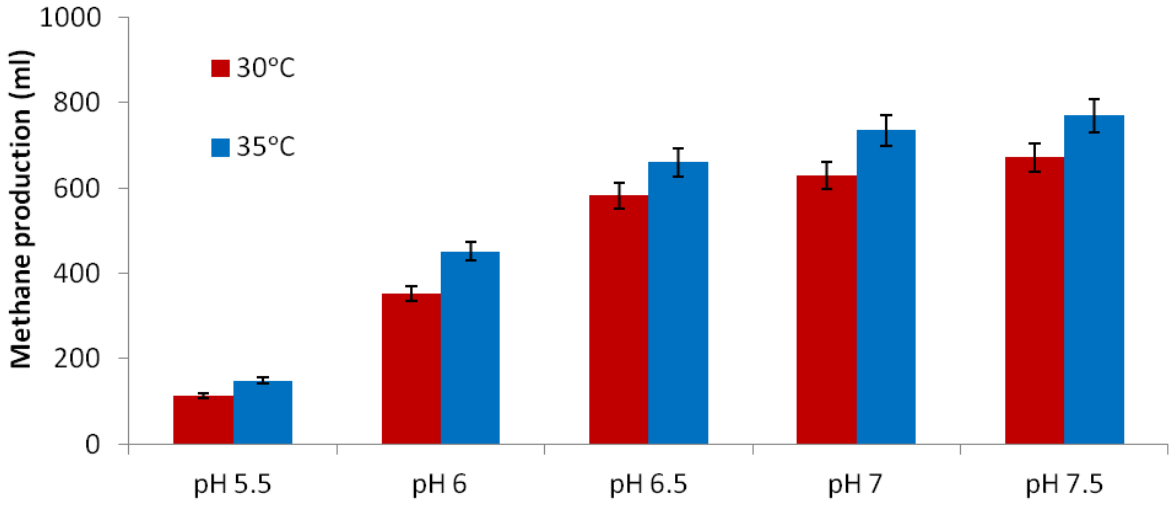


Fig. 4.18: Effect of temperature on methane generation in samples without CO_2 injection with the CTMP wastewater

Figures 4.19 and 4.20 show the effect of temperature on methane generation at different operational pH in the presence and absence of CO_2 injection, respectively, for the recycled paper wastewater. Temperature has a significant impact on methane generation at all operating pH values. Regardless of CO_2 injection, more methane was generated at 35ºC compared to 30ºC. This observation is attributed to the higher methanogenic activity at 35ºC compared to 30ºC. For

example, at pH 5.5-7.5 and in the presence of CO_2 injection methane generation was 17-25 ml (15±3%) higher at 35ºC compared to the volume produced at 30ºC.

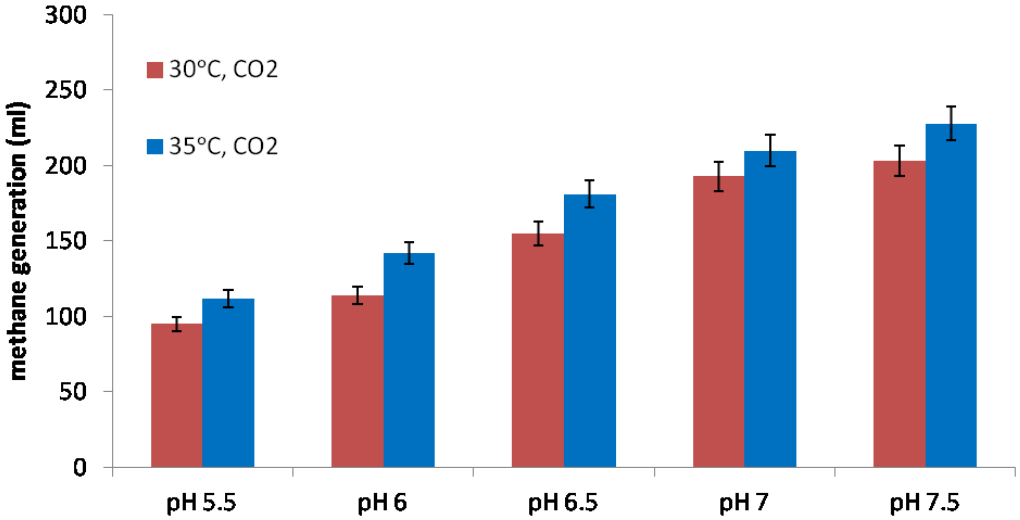


Fig. 4.19: Effect of temperature on methane generation in samples with CO_2 injection in the recycled paper wastewater

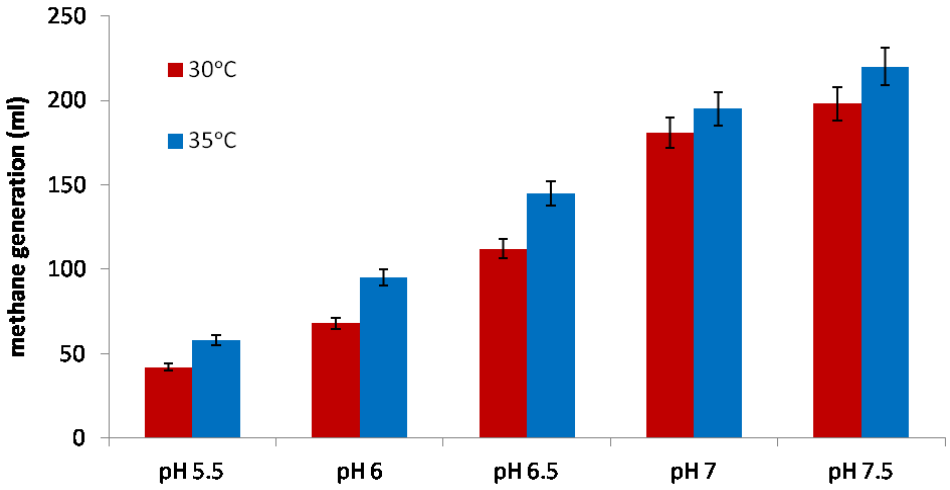


Fig. 4.20: Effect of temperature on methane generation in samples without CO_2 injection in the recycled paper wastewater

4.1.4.3 Methane production yield

Figures 4.21 and 4.22 show methane production yields (methane production per COD removal) at different operating conditions for CTMP and recycled paper wastewaters, respectively. It can be observed that when the temperature is kept constant, methane production per COD removal is higher at higher pH values. Temperature had a direct effect on methane production yield and at higher temperatures more methane was generated per specific mass of COD removed. Injection of carbon dioxide is another parameter that can increase the methane production yield. The parameters that contribute to higher methane production yield are the same as parameters that govern higher methane production.

The theoretical yield for methane production per COD removal at standard conditions (T=0ºC, P=1 atm) is 0.35 L methane/g COD removed (Manhokwe et al., 2009). By applying the ideal gas rule ($P_1V_1/T_1=P_2V_2/T_2$) the theoretical value was calculated for the conditions applied in this project. This value is equal to 0.388 and 0.395 L methane /g COD removed at 30 and 35ºC, respectively. The theoretical value can be obtained when the efficiency of COD conversion to methane is 100%. As a result, the conversion efficiency of the system can be evaluated by comparing its methane generation yield with the theoretical value. The experimental system has a higher efficiency when the obtained yield is closer to the theoretical value.

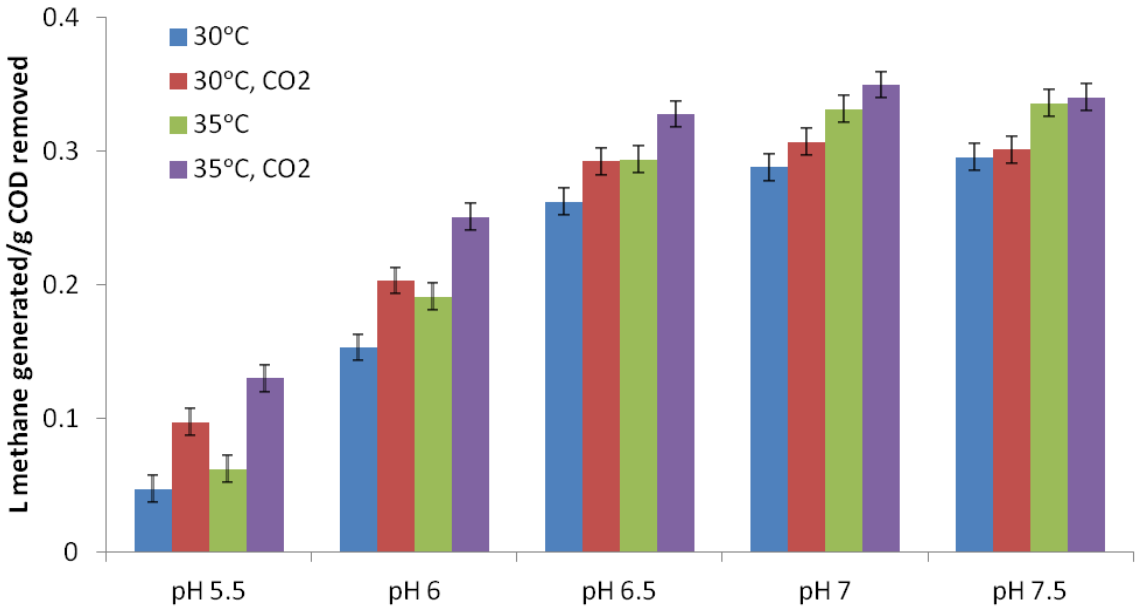


Fig. 4.21: Effect of temperature, pH and CO_2 injection on methane production yield with the CTMP wastewater

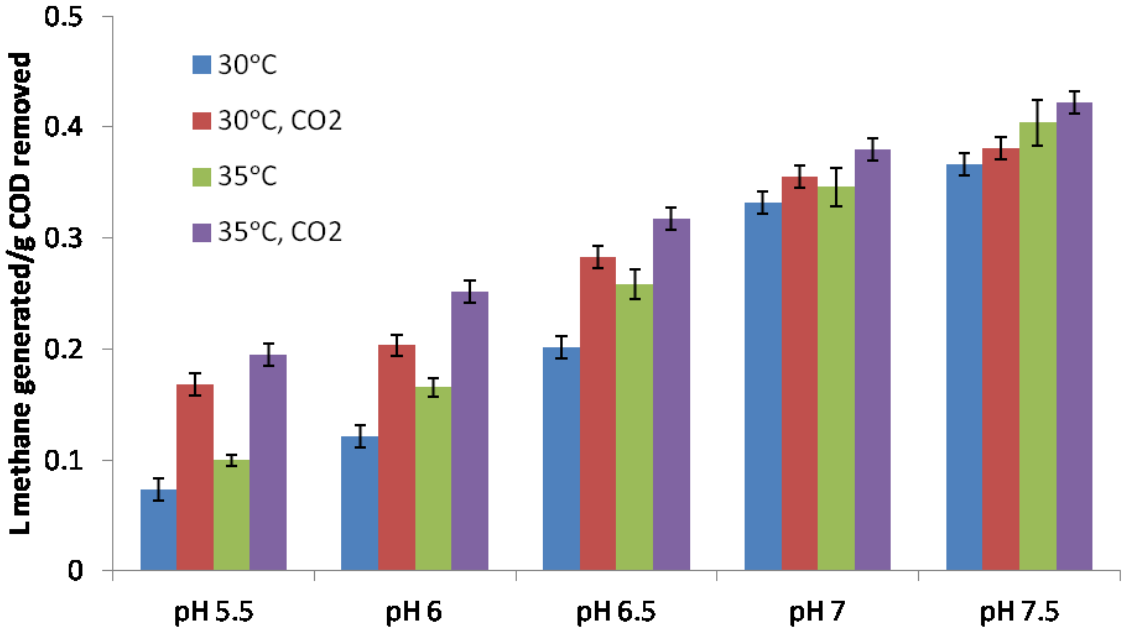


Fig. 4.22: Effect of temperature, pH and CO_2 injection on methane production yield with recycled paper wastewater

By comparing Figures 4.21 and 4.22, it can be observed that although methane generation in the CTMP wastewater was higher than that in the recycled paper wastewater, the experimental methane generation yield in the recycled paper wastewater is more than that obtained in the CTMP wastewater and its value is closer to the theoretical value. For example, the minimum methane generation yield in the recycled paper wastewater belongs to the samples at pH 5.5, 30°C, and without CO_2 injection which was 0.07 L methane/g COD removed, while the maximum amount at 35°C and pH 7.5 and in the presence of CO_2 injection was 0.42 L methane/g COD removed. For the CTMP wastewater, the minimum and maximum methane generation yields were respectively equal to 0.05 and 0.34 L methane/g COD removed. The lower methane generation yield in the CTMP wastewater is related to the condition of biomass used with this wastewater. The biomass for recycled paper wastewater was used right after it was received from the treatment plant. However, for the CTMP wastewater, the biomass was used after two years of storage in the fridge. The lower methane generation yield observed in the CTMP wastewater may be linked to the addition of chemicals in the CTMP production plant (Ekstrand et al., 2013).

4.2 Continuous operation

4.2.1 COD removal efficiency

During the continuous operation, five deliveries of wastewater were received from the Tembec WWTP in Quebec, with initial COD concentrations of 10200, 6540, 6740, 7285, 9500 mg/l. Figure 4.23 show the percentage removal of COD at different organic loading rates for the continuous experiments in the R_1 and R_2 reactors. The results show that pH adjustment in R_1 or CO_2 injection in R_2, compared to R_1 which did not receive any CO_2 injection, did not affect the COD removal efficiency. However, by increasing the organic loading rates and decreasing the hydraulic retention time, the COD removal efficiency decreased gradually from 70% at HRT = 6 d and reached 65% at HRT = 2 d. This is because of the shorter contact time of biomass and wastewater at higher OLR (Leong and Nur, 2011).

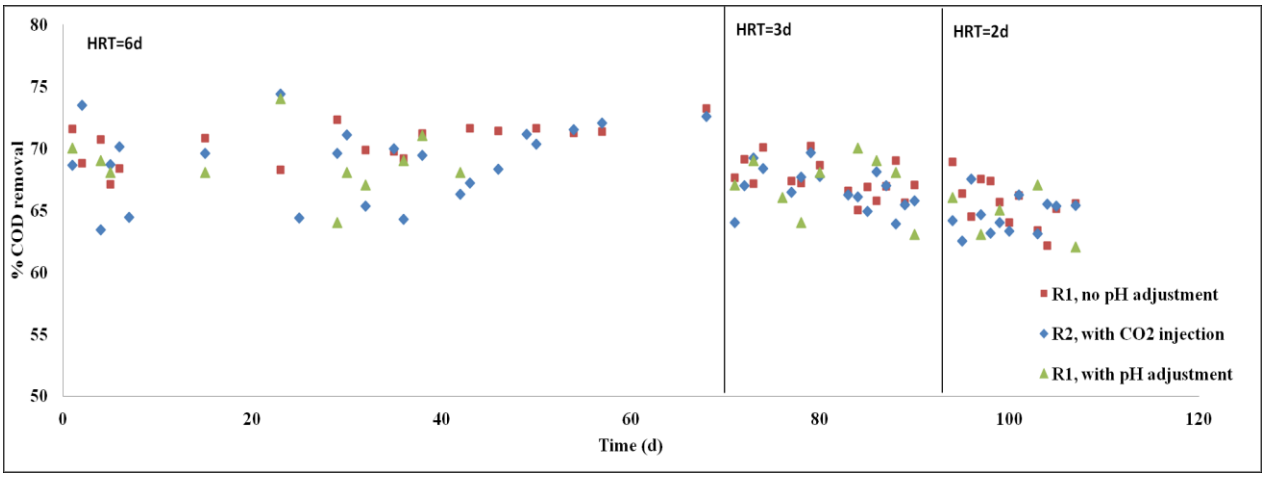


Fig 4.23: COD removal efficiency at different HRT values in R_2 and R_1 with and without pH adjustment

4.2.2 BOD removal efficiency

Figure 4.24 presents the result of BOD removal at the examined OLR conditions from R_2 (with CO_2 injection) and R_1 (control) with and without pH adjustment. During the continuous operation, the BOD removal efficiency in R_2 with CO_2 injection, decreased from 89% to 82% when the OLR increased from 1 to 3 g COD/l.d. The control reactor without CO_2 injection

showed a similar trend in the BOD removal efficiency which shows that the saturation of wastewater with CO_2 does not affect the BOD removal. Similar to the results of COD removal efficiency, the observed reductions in the BOD removal efficiency was because of lower contact time of biomass and wastewater at higher OLR conditions (Leong and Nur, 2011). Although the increase of OLR from 1 to 3 g COD/l.d, reduced the removal efficiencies of BOD and COD, the effect was insignificant for COD and BOD removal, in the range of 5±1%.

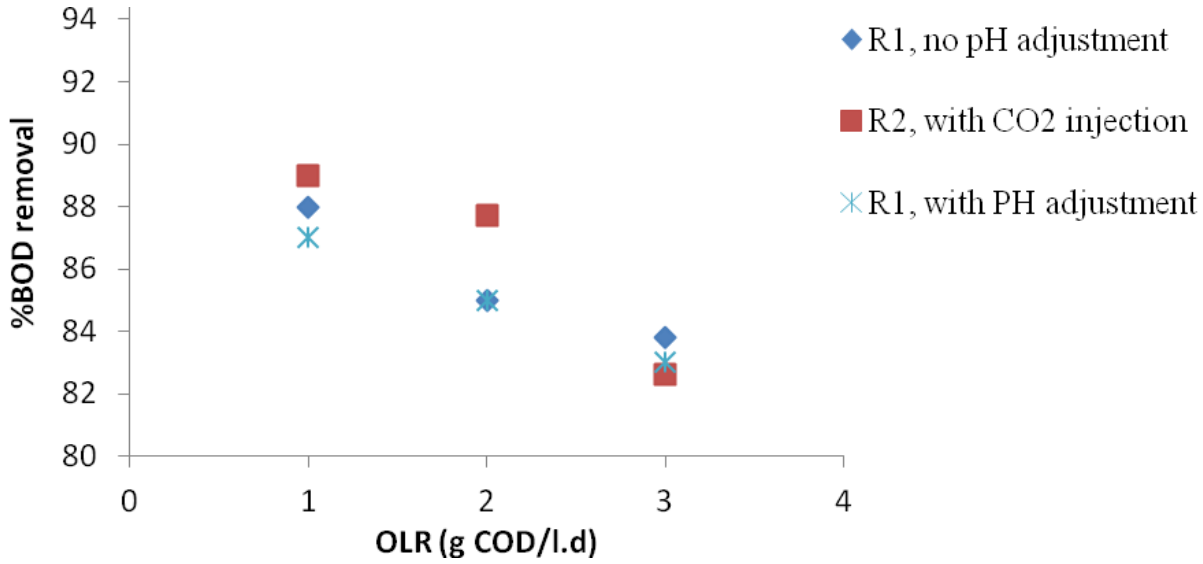


Fig 4.24: BOD removal efficiency at different HRT values in R_2 and R_1 with and without pH adjustment.

4.2.4 pH and alkalinity

The dissolved carbon dioxide concentration in the wastewater was calculated by indirect approaches using the liquid pH and alkalinity (Alimahmoodi et al., 2008). According to equations 3.3-3.6, lower pH and higher alkalinity values indicate higher dissolved carbon dioxide concentrations.

The initial wastewater (influent of control reactor, R1 without pH adjustment) had the initial pH of 6.5±0.1. CO_2 injection into the R_2 influent decreased its pH to 5.5±0.1. However, the injection of CO_2 had no effect on the alkalinity; hence the influent of R1 without pH adjustment and R_2 with CO_2 injection had similar alkalinities. By injecting CO_2 into the wastewater, the equilibrium between carbonic compounds (Eq. 3.4) shifts to the right, resulting in a higher consumption of

dissolved CO_2 and higher production of bicarbonate and carbonate ion and H^+ which is associated with the decrease of the liquid pH. On the other hand, the alkalinity remains constant since the overall reaction produces the same equivalent number of positive (H^+) and negative (HCO_3^- and/or CO_3^{2-}) ions that participate in the production of alkalinity, as shown in equations 4.1 and 4.2.

At neutral pH values: $CO_2 + H_2O \rightarrow HCO_3^- + H^+$ (4.1)

At high pH values: $CO_2 + H_2O \rightarrow CO_3^{2-} + 2H^+$ (4.2)

In the control reactor (R_1 with pH adjustment), the influent wastewater pH was adjusted to pH 5.5 (similar to R_2 reactor with CO_2 injection) by the addition of sulfuric acid. However, this influent had a lower alkalinity compared to the R_2 feed, which results in a lower concentration of dissolved carbon dioxide in the influent of R_1 with pH adjustment. Alkalinity is defined as the capacity of wastewater to neutralize acid. When acid is added to the wastewater in the influent of control reactor (R_1 with pH adjustment), the reaction of carbonic compounds shifts to the left to consume H^+. Consequently, the carbonate and bicarbonate ions concentrations decrease, resulting in the decrease of alkalinity.

Figures 4.25 and 4.26 show the variations of pH and alkalinity in the effluents of R_1 and R_2 reactors. The effluents of R_1 and R_2 had similar alkalinity and pH values. The calculated dissolved CO_2 concentrations in the influents and effluents of R_1 and R_2 reactor, based on the liquid pH and alkalinity, were used in the CO_2 mass balance equations to estimate the extent of CO_2 conversion to CH_4.

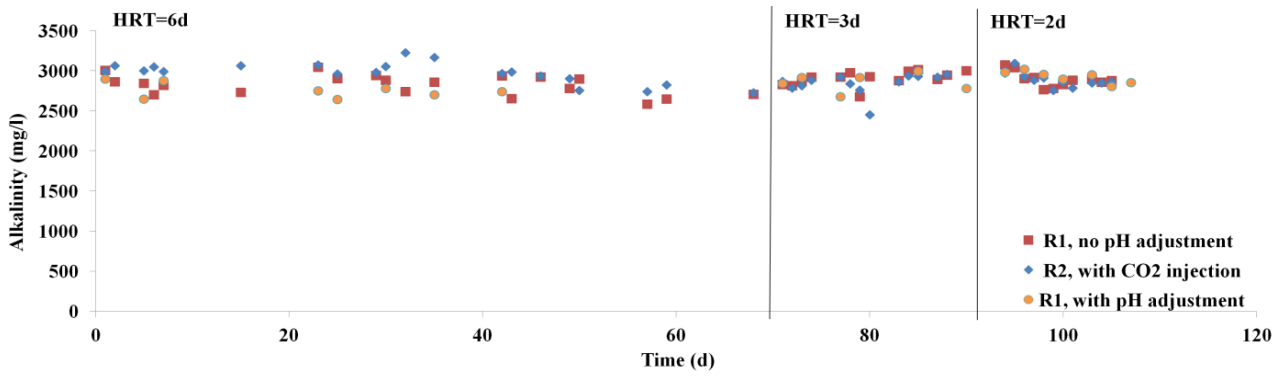


Fig. 4.25: Effluent alkalinity at different HRT values in the R_2 and R_1 with and without pH adjustment

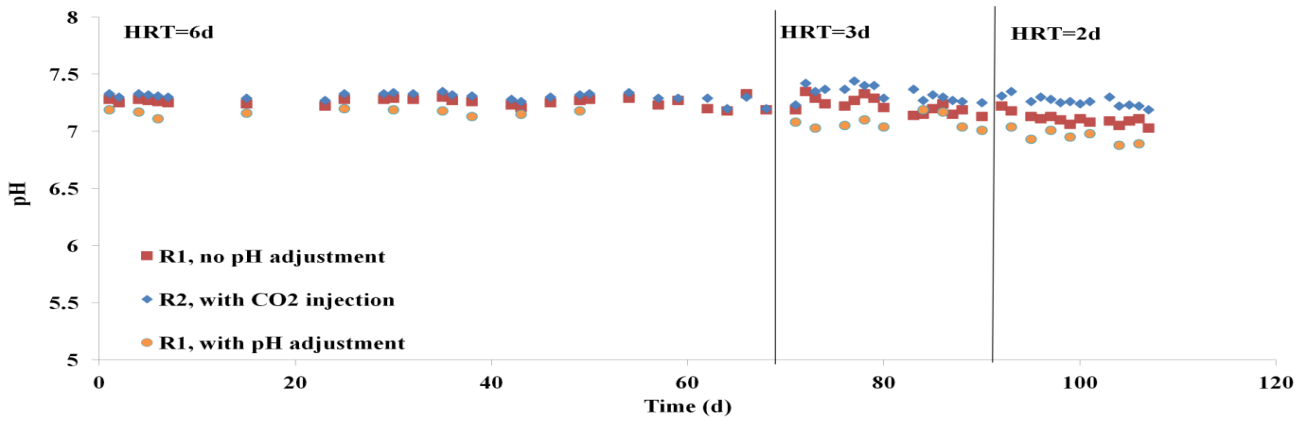


Fig. 4.26: Effluent pH at different HRT values in the R_2 and R_1 with and without pH adjustment

4.2.5 Methane generation and concentration in gas phase

During the continuous operation, methane generation in R_1 (control reactor without pH adjustment) increased by increasing the OLR. This was expected since the higher OLR condition implies the introduction of a higher amount of COD and organic substances into the bioreactor, resulting in a higher removal of organic matter and higher generation of methane (Alimahmoodi et al., 2008). However, in the R_2 setup with CO_2 injection, the increase of OLR initially resulted in a higher CH_4 generation which was followed by a decrease in its generation. This phenomenon is observed since in the R_1 setup without pH adjustment, the pH of influent was equal to the initial pH of wastewater (pH 6.5), while the influent to R_2 was saturated with CO_2 and had a lower pH of 5.5. Considering that the optimum pH for methanogenic activity is 6.5-7.5, the pH in R_2 influent was considerably lower than the optimum value and produced an unfavorable condition for bacterial activities which is similar to the trend previously reported in the literature (Alimahmoodi et al., 2008). As the organic load to the R_2 reactor increased, at first the bacteria received substrate supply at a higher rate which resulted in a higher rate of methane generation. However, as the pH condition was not appropriate for the growth and activities of methanogenic bacteria, a gradual decrease of CH_4 generation occurred. As a result, the CH_4 content of biogas decreased (Fig. 4.28).

It should be noted that the pH increased during the anaerobic treatment after the consumption of volatile acids and carbon dioxide in the reactors. At different OLR values, regardless of the influent pH, the effluent wastewater from the R_1 and R_2 reactors had a pH of 7.1±0.3 which is an appropriate pH for methanogenic activity. However from the results presented in Figures

4.27and 4.28, the pH of the influent to R_1 and R_2 reactors showed a significant effect on methane generation and methane content in the biogas. Methane generation was lower when the influent pH was 5.5 compared to 6.5. In order to investigate this observation, pH of the wastewater from the top and the bottom of the reactors was measured which showed different values. A lower pH was observed at the bottom of reactors which was less favorable for methanogenic activity. The liquid pH increased gradually as it approached the top of reactor due to consumption of the VFAs. Considerable stratification inside the reactors was the result of different bacteria at the influent and the effluent. The influent still had mainly acidifying bacteria while there was more methanogenic bacteria towards the effluent. The low mixing in the UASB reactors caused the pH not to be evenly distributed. The wastewater entered the reactor from the bottom and exited from the top corner. There were no mechanical mixing in the reactors and the only mixing was generated by gas generation in the reactor. This effect was more important at the higher examined OLR values where higher amounts of wastewater per unit of time entered into the reactor. Under these conditions, less time for mixing of the wastewater was provided, resulting in a higher stratification and less methanogenic activity when the influent pH was 5.5. The pH at the bottom of R_1 reactor without pH adjustment was 7 to 6.8±0.1 corresponding to the OLR of 1-3 g COD/l.d, respectively, while this value in R_2 and R_1 with pH adjustment was between 6.6 and 6.1±0.1. It should be noted that methanogenic activity is higher over the pH range of 6.6–7.8 (Lay et al., 1997).

In order to eliminate the effect of pH and make the effect of CO_2 saturation of wastewater apparent, another continuous experiment was performed in which the pH of influent to the control reactor (R_1) was adjusted to 5.5 (by the addition of sulfuric acid) to have the same pH as the R_2 influent with CO_2 injection. The results of methane generation are presented in Figure 4.27. Methane generations in R_2 at OLR 1, 2 and 3 were approximately equal to 400-570, 960-1120, and 700-1700 ml/d, respectively, while these values for R_1 reactor with pH adjustment were approximately equal to 200-300, 460-700, and 370-920 ml/d. The higher methane generation in R_2 compared to R_1 with pH adjustment is attributed to the bioconversion of CO_2 to methane.

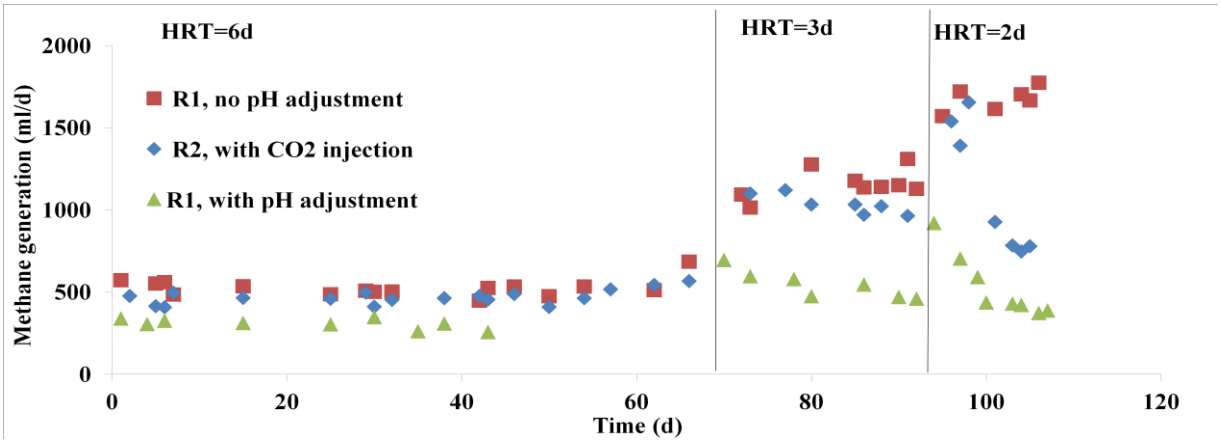


Fig. 4.27: Methane generation at different HRT values in R_2 and R_1 with and without pH adjustment

Methane contents of the generated gas from R_1 and R_2 reactors are shown in Figure 4.28 which demonstrates approximately 77±2% methane content of the produced gas from the control reactor without pH adjustment (R_1). This value was almost constant at different organic loading rates examined. However, the methane content of the generated gas from R_2 with CO_2 injection in the feed, and R_1 with pH adjustment in the feed (with the pH of feed at 5.5 in both reactors) was approximately 76±2% at the OLR=1g COD/l.d and respectively decreased to 69 and 66% at the OLR=2 and 60 and 57% at the OLR= 3 g COD/l.d. This observation showed the effect of influent pH on the methane content of the generated gas. This effect was higher at higher OLR values because of the lower mixing of the influent wastewater with the bulk wastewater in the reactor, as explained before.

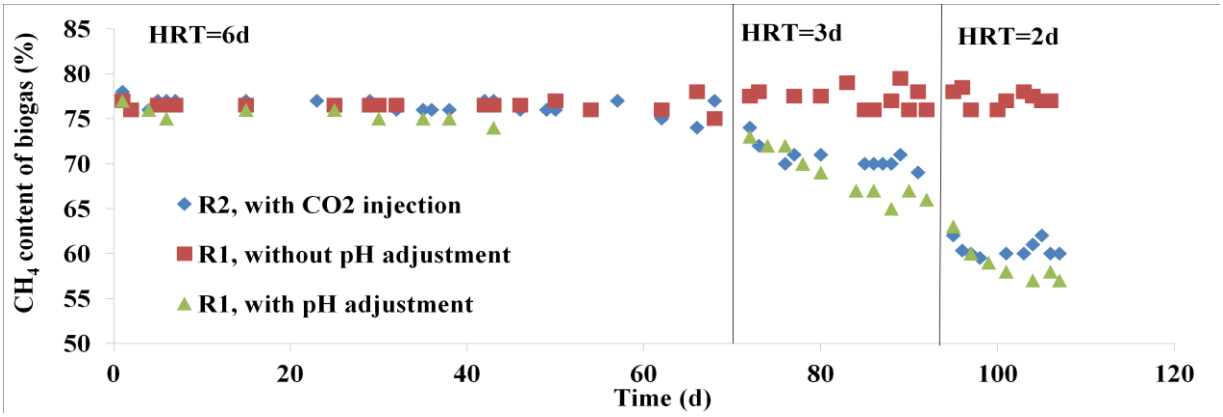


Fig. 4.28: Methane content of biogas at different HRT values in R_2 and R_1 with and without pH adjustment.

4.2.6 Methane generation per COD removal

As mentioned earlier, the wastewater samples received from Tembec had different COD concentrations. Therefore, in order to maintain the consistency of reporting, methane generation was calculated in terms of L CH_4 generated/ g COD removed. As shown in Figure 4.29, methane generation/ COD removal is closer to the theoretical value (0.395 L methane /g COD removed at 35ºC and 1atm) in R_2, in which the influent wastewater was saturated with CO_2, compared to R_1 (the control reactor with pH adjustment). For example, the average methane generation yields in R_1 with pH adjustment at OLR of 1 to 3g/l.d were 0.18, 0.12, and 0.086 L CH_4/g COD_{rem} respectively, while these values for R_2 were in average 0.25, 0.24, and 0.17 L CH_4/g COD_{rem} respectively. These values correspond to approximately 38 to 100% increase in methane generation yields in R_2 compared to R_1 with pH adjustment. Higher efficiency of R_2 for methane generation compared to R_1 with pH adjustment confirms the conversion of CO_2 to methane in R_2. The reductions in methane generation in R_2 and in R_1 with pH adjustment compared to R_1 without pH adjustment were because of the unfavorable pH condition in these two reactors.

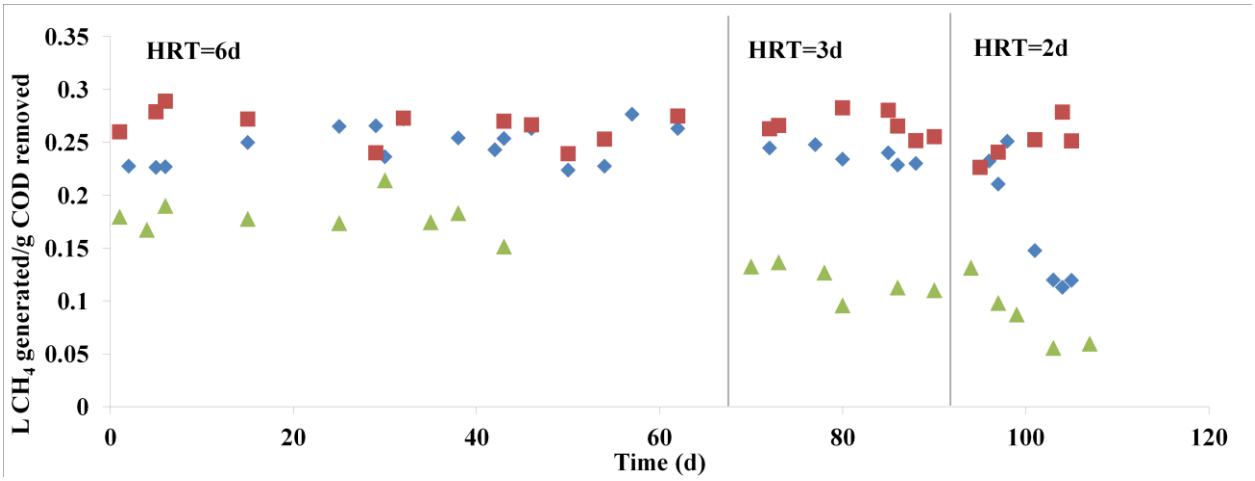


Fig. 4.29: Methane generation per COD removal at different HRT values in R_2 and R_1 with and without pH adjustment.

4.2.7 Carbon dioxide fate

Table 4.1: Sample calculations for CO_2 fractions participating in different pathways

Parameter	Symbol	Formula
pH	A	A
Alk (mg/l as $CaCO_3$)	B	B
HCO_3^-/CO_3^{2-}	C	$F/(4.68 \times 10^{-11})$
Alk (eq/l as $CaCO_3$)	D	$(0.01998 \times B)/1000$
$[OH^-]$ (M)	E	$10^{-14}/F$
$[H^+]$ (M)	F	10^{-A}
Alk-$[OH^-]$+$[H^+]$	G	$D - E + F$
$[CO_3^{2-}]$ (M)	H	$G/\{2 + [F/(4.68 \times 10^{-11})]\}$
$[CO_2]$ (M)	I	$(H \times F^2)/(2.11 \times 10^{-17})$
CO_{2f} (mg/l)	J	$I \times 44000$
$[HCO_3^-]$ M	K	$C \times H$
$[CO_2]$+ $[HCO_3^-]$+$[CO_3^{2-}]$	L	$K + I + H$
($[CO_2]$+$[HCO_3]$+$[CO_3^{2-}]$)*44000 (total final carbonic compounds as mg/l CO_2)	M	$L \times 44000$
CO_{2i} (mg/l)	N	N
total initial carbonic compounds as mg/l CO_2	O	O
CO_2 in biogas (mg /l)	P	P
CO_2 removed or converted to other types (mg/l)	Q	$N - J - P$
%CO_2 removed or converted to other types	R	$Q \times 100/N$
mg/l all types removed=mg/l CO_2 removed	S	$O - M - P$
mg/l CO_2 converted	T	$Q - S$
%all types removed	U	$S \times 100/O$
%CO_2 converted to other types	V	$(Q - S) \times 100/N$
%CO_2 removed	W	$R - V$
% CO_2 in biogas	X	$P \times 100/N$
% no change	Y	$100 - (Y + W + V)$

Similar to the batch test, the fate of carbon dioxide during the continuous operation was evaluated and the amount of CO_2 that participated in different pathways was calculated as explained in Chapter 3. Detailed formula for these calculations is presented in Table 4.1.

Figure 4.30 presents the CO_2 fractions participating in different pathways at different HRT values in R_2 with CO_2 injection and R_1 (control reactors with and without pH adjustment). In this figure, at each OLR, the bars from left to right are respectively related to the control reactor without pH adjustment, control reactor with pH adjustment, and reactor with CO_2 injection. The extent of CO_2 removal is presented on each bar and the concentrations of dissolved CO_2 in the influent of each reactor are presented on top of each bar.

Figure 4.30 shows that approximately 83-97% of the injected dissolved CO_2 in R_2 is participated in the removal pathways. For example, at the OLR=2g COD/l.d the injected dissolved CO_2 in R_2 is equal to 1406 mg/l (6674-5268=1406 mg/l), of which 97% (4253-2883=1370 mg/l) was removed by various pathways. The generated methane in the anaerobic treatment is the results of COD removal or CO_2 conversion into methane. In order to determine the contribution of CO_2 conversion into methane to the total CO_2 removal, the equivalent CO_2 removal of the generated methane was calculated. By comparing the results of methane generation yield in Fig. 4.29 and CO_2 removal in Fig. 4.30, it can be concluded that not all the removed carbon dioxide was converted to methane. A portion of dissolved CO_2 was involved in precipitation reactions or in other chemical reactions different from the conversion to carbonic compounds. However, comparing the increase in methane generation yield and CO_2 removal shows that approximately all the excess CO_2 removal in R_2 compared to R_1 at the same pH was due to the conversion to methane. This conclusion was made by estimating the equivalent CO_2 removal corresponding to the increased methane generation yield as a result of CO_2 injection in R_2, followed by the comparison of this value with the experimental value of the excess CO_2 removal in R_2 compared to R_1 at the same pH value. In order to calculate the amount of CO_2 that is equivalent to the increase in methane generation yield as a result of CO_2 injection in R_2, initially the increase in methane generation yield in R_2 was multiplied by the COD removal/d which gives the excess L CH_4 produced/d as a result of CO_2 injection. The equivalent CO_2 can be obtained by assuming that one mole of CO_2 can be converted to one mole of CH_4.

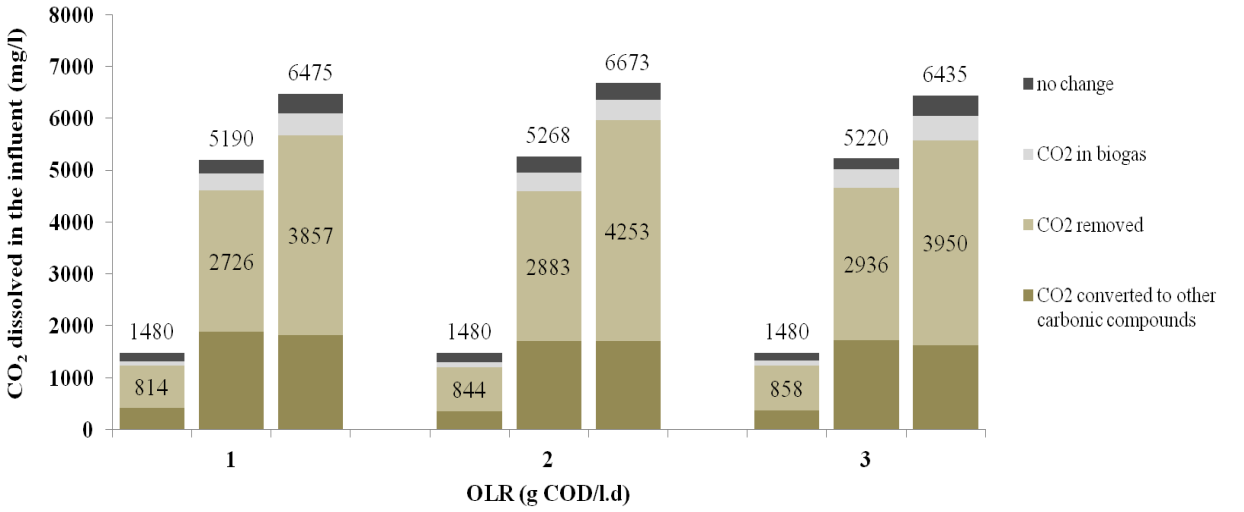


Fig. 4.30: CO_2 fractions participating in different pathways at different HRT values. At each OLR, the bars from left to right are related to R_1 without and with pH adjustment and R_2

4.2.8 Microscopic image and SEM photos

The microscopic images of the granular sludge used as the inoculum and during the operation of R_1 and R_2 reactors are presented in Figure 4.31 with 50X enlargement. The photos show that the size and shape of granules in R_1 and R_2 reactors and the inoculum are all similar. Figure 4.32 shows a closer image of the bacteria inside the granules (1000X). This photo is taken in a dilute medium in order to see the bacterial cells separately.

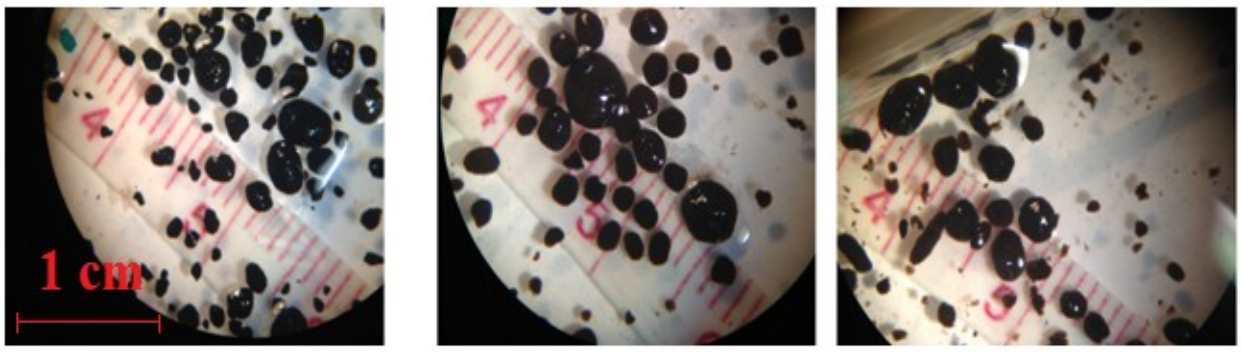


Fig 4.31: Microscopic image of the biomass used in this project. From left to right: initial biomass, biomass in R_1, and R_2.

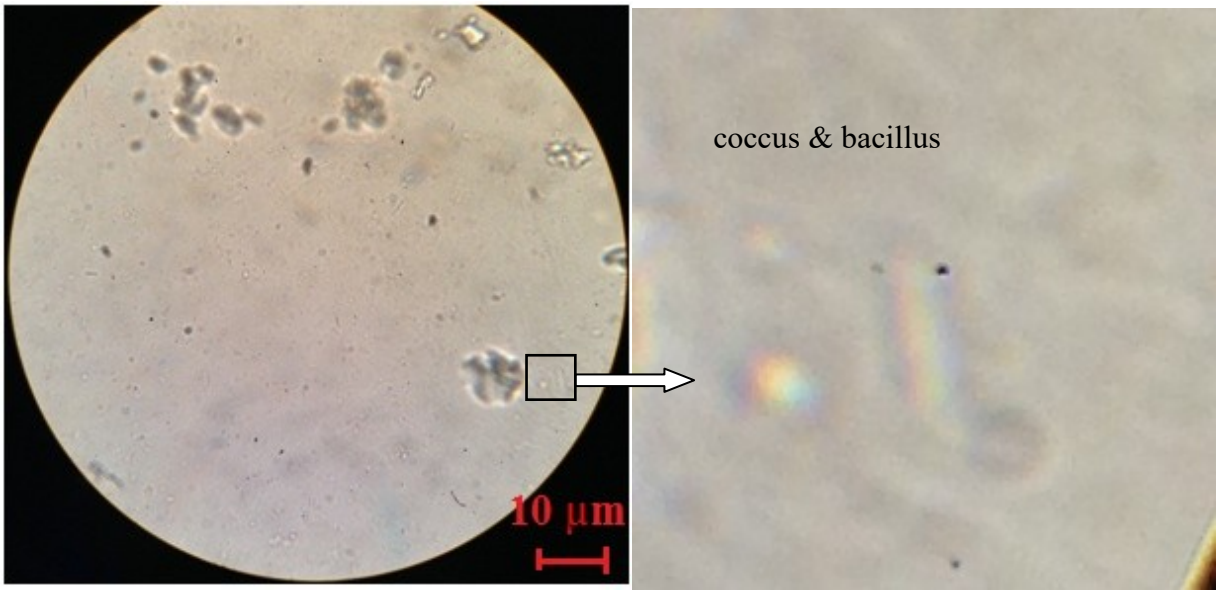


Fig 4.32: Microscopic image of the bacteria inside the granules (1000X)

Scanning electron microscopy (SEM) image of the bacteria are presented in Figure 4.33. For taking the bacterial images from the R_1 and R_2 reactors, the liquid from the top of granules was used and gold coating was applied as part of the procedure. The initial biomass photo is taken from the solid granules and therefore shows a higher density of bacteria. In both R_1 and R_2 reactors, different types of coccus and bacillus bacteria were observed (Figure 4.33).

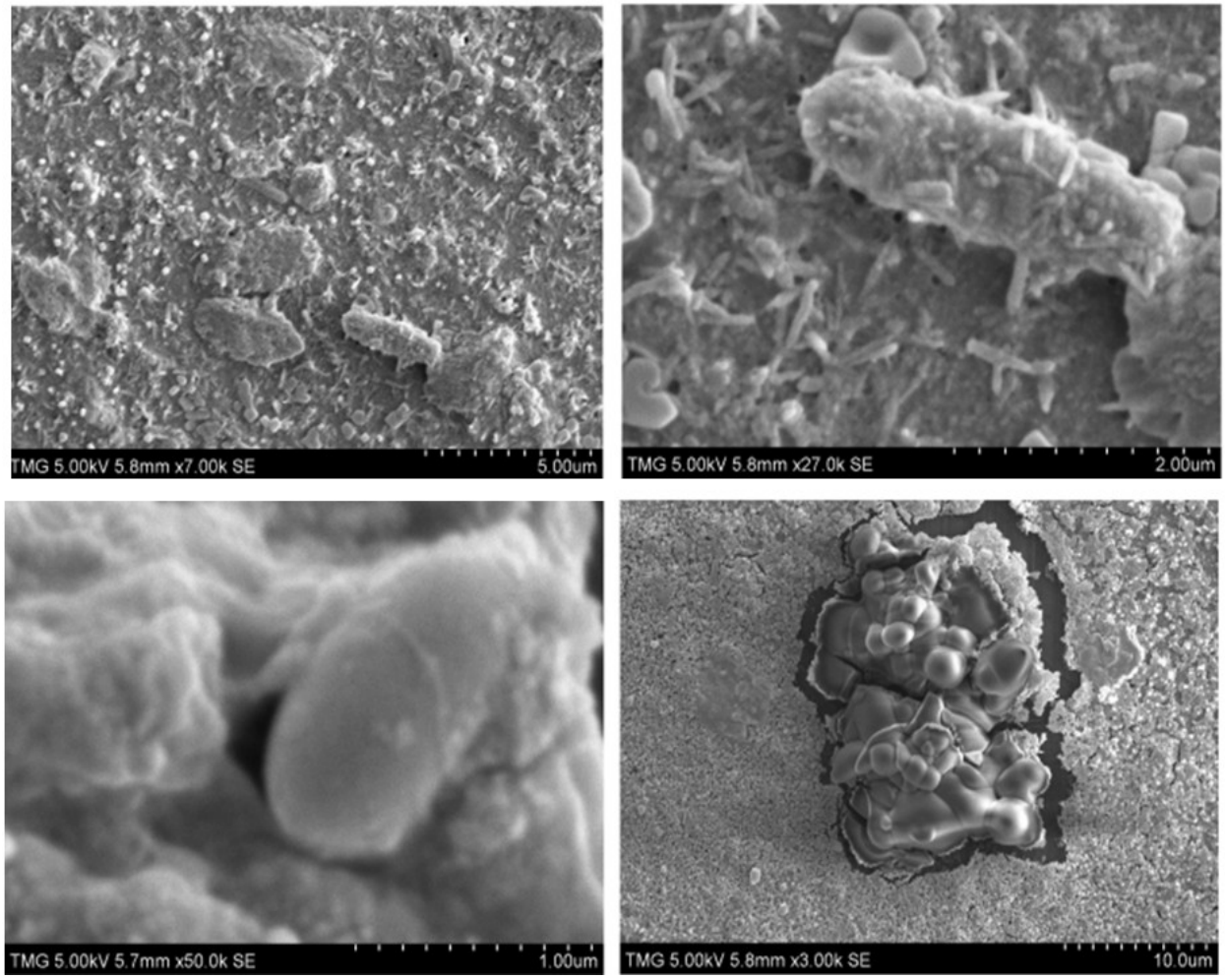


Fig 4.33: SEM image of biomass; top left and right: Biomass in R_2, bottom left: Biomass in R_1, and the bottom right: initial biomass

4.3 Kinetic Study

Two sets of data were used in the kinetic study: the first set of data was obtained from the batch experiments in a 1-L container using the Cascades recycled paper wastewater, and the second set was obtained from the 5-L reactor operation in batch mode using the CTMP wastewater. The estimated values of kinetic parameters are presented in Table 4.2.

Table 4.2: Values of kinetic parameters

Parameter	Cascades wastewater	CTMP wastewater
X0 (g/L)	30	25
S0 (g/L)	2.2	11
μ_m (1/d)	0.02	0.025
K_s (g/L)	0.4	0.6
k_d (1/d)	0.3	0.5
Y(g/g)	0.015	0.01

Figures 4.34 and 4.35 present the experimental data and simulated values of COD concentration during batch operations using the Cascades recycled pulp and paper wastewater at 35°C and 30°C, respectively. Similar patterns were observed during all operating conditions.

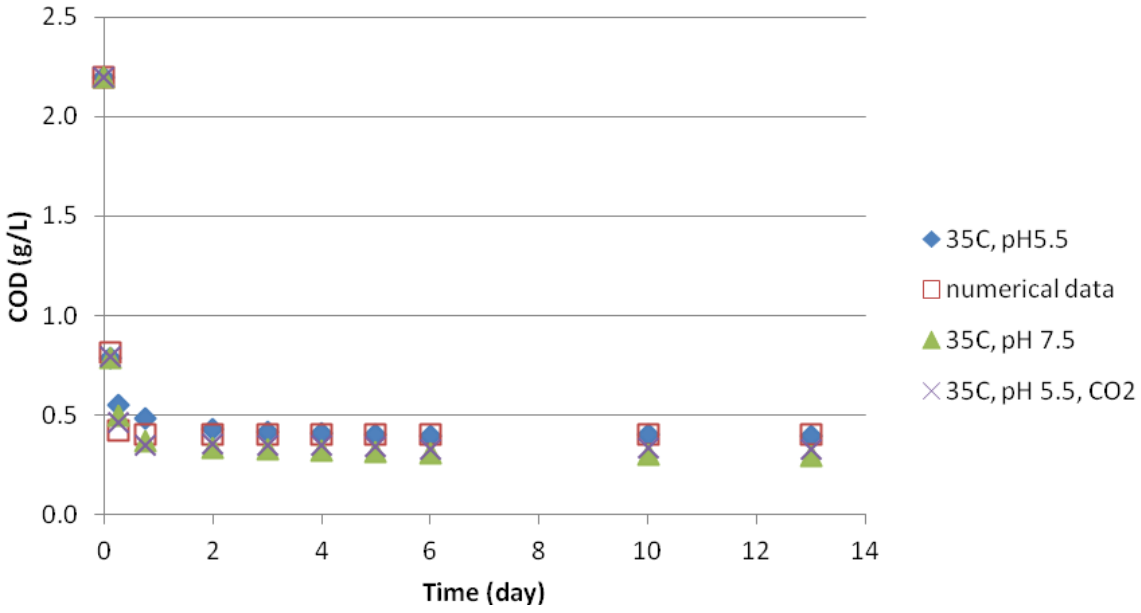


Fig. 4.34: Comparison of experimental data and simulated values at 35°C

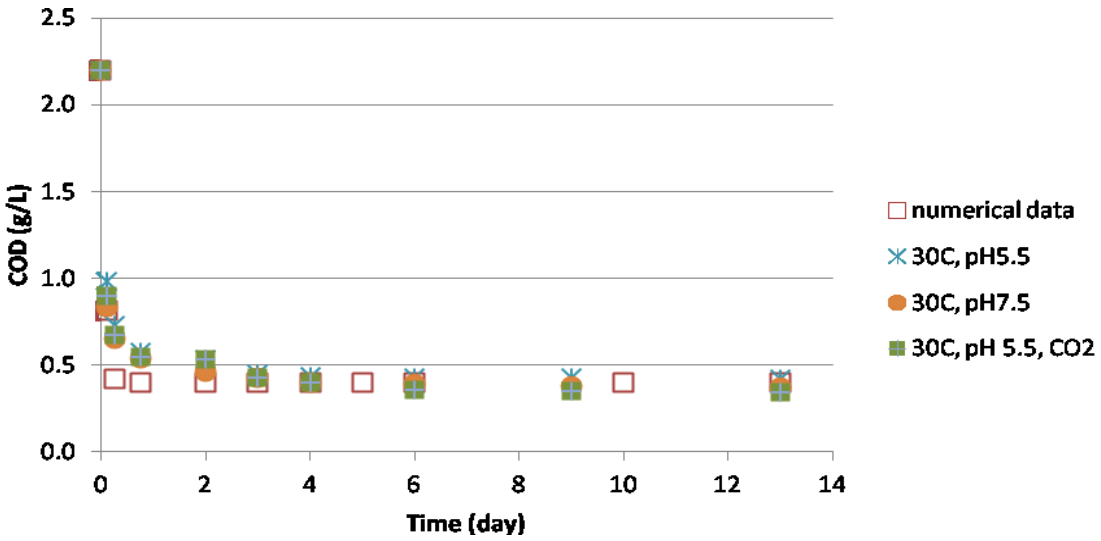


Fig. 4.35: Comparison of experimental data and simulated values at 30°C

As shown in Table 4.2, the values of kinetic parameters estimated from the two experimental setups were very close. The higher value of K_s estimated from the results of batch operation in the 5-L reactor operation possibly reflects the long-term storage of bacteria in the refrigerator at 4°C before use, while the bacteria that initiated the batch operation in 1-L bottles with the recycled paper wastewater were not stored in the fridge. Figure 4.36 shows the comparison of simulated values and experimental data of the reactor during the batch operation.

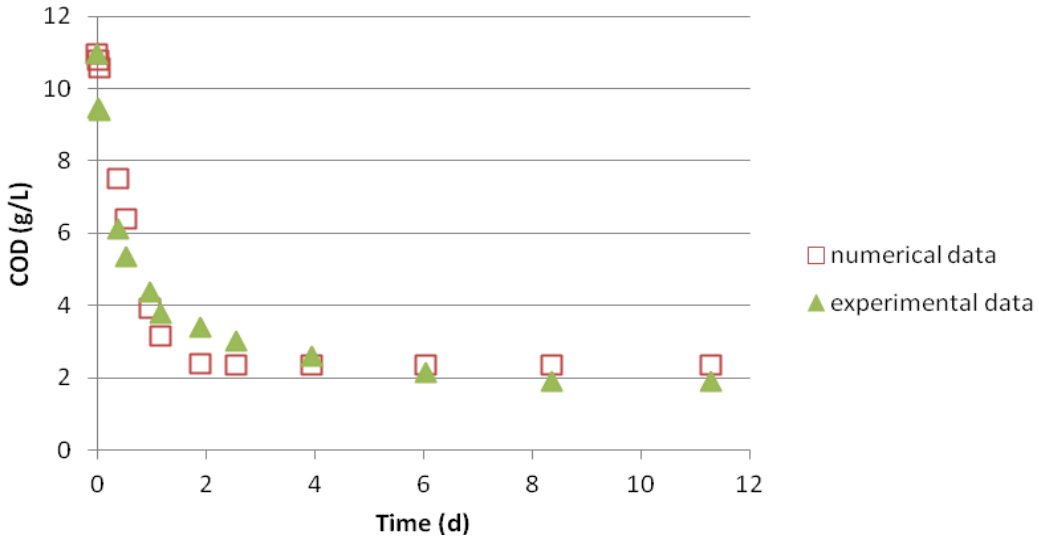


Fig. 4.36: Comparison of numerical values and experimental data in the UASB reactor during the batch operation

4.4 Comparison with other anaerobic treatment systems for pulp and paper wastewaters

Each pulp and paper mill has a particular wastewater composition that depends on the pulping process, used chemicals, age of the mill, and handling of raw materials (Habets, 2012). In the pulp and paper industry, depending on the source of effluent, the COD removal efficiency is in the range between 30 and 90%, and the methane generation yield is in the range of 0.3 and 0.4 m^3/kg COD removed (Meyer and Edwards, 2014). Table 4.3 shows a comparison of composition and anaerobic digestibility of different pulp and paper mill streams. Based on the literature reviews, for recycled paper wastewater the methane generation yield is in the range of 0.24-0.4 m^3CH_4/kg COD removed. However the results of batch tests on the recycled paper wastewater in the present study showed that in the presence of CO_2 injection the methane generation yield up to 0.42 m^3CH_4/kg COD removed was achieved. For the CTMP wastewater, literature review shows the methane generation yield is in the range of 0.18-0.31 m^3CH_4/kg COD removed. However, the results of the batch tests in the present study showed up to 0.34 m^3CH_4/kg COD removed. With regards to the importance of methane as a biogas and removal of CO_2 as a GHG, this is an outstanding result to produce more methane simultaneously by removal of CO_2.

Table 4.3: Comparison of composition and anaerobic digestibility of different pulp and paper mill streams.

Type of wastewater	COD concentration (g/l)	%COD removal	Methane generation yield (m^3/kg COD_{rem})	Reactor type	Reference
Recycled paper mill effluent	0.6-15	58-86	0.24-0.40		Maat, 1990; Paasschens et al., 1991; Mermillod et al., 1992; Driessen et al., 1999
Recycled paper mill effluent	3.3	75	0.35	UASB	Mermillod et al., 1992
Recycled paper whitewater	32	85-90	-		Alexandersson and Malmqvist, 2005; Latorre et al., 2007
Recycled paper mill effluent	0.14-2.8	65	~0.3	UASB	Paasschens et al., 1991
TMP/CTMP	4.0-7.2	30-40	-	UASB	Habets and de Vegt (1991)
CTMP	7.5-10.4	45	0.18-0.31	Pilot	Habets and de Vegt, 1991
CTMP	6.0-10.4	45-66	0.18-0.31		Welander and Anderson, 1985; Habets and de Vegt, 1991; Cornacchio, 1989
CTMP	4.5-11	65	0.4	UASB	Tembec, Matane, 2015
CTMP	6.5-10.2	65-70	0.086-0.18 R_1 with pH adjustment 0.17 -0.25 R_2 0.23-0.3 in R_1 without pH adjustment	UASB, lab scale	Present study
CTMP	9.1	80-88	0.05-0.34	Batch test	Present study
Recycled paper mill wastewater	2.2	80-88	0.07-0.42	Batch test	Present study

Chapter 5: Cost Estimation and GHG Analysis

Fig. 5.1: Tembec Matane WWTP (Web 5)

The CTMP wastewaters used in the present research are high strength wastewaters that were received from Tembec Matane (Fig. 5.1) at different times with different COD values in the range of 6.5-10.2 g/l. Tembec plant uses conventional hybrid (anaerobic/aerobic) treatment systems (More information about the plant is available in Appendix B). The cost estimation and GHG analysis was done for Tembec hybrid treatment system based on the information that they provided as well as data from literature reviews. The economic feasibility of the developed treatment process in the present study to treat wastewaters from the pulp and paper industry was evaluated by assuming the application of this system in Tembec treatment plant and considering that aerobic treatment follows the anaerobic treatment (developed hybrid treatment system) and

comparing the cost and GHG generation related to the developed hybrid treatment system with conventional hybrid treatment system as well as aerobic treatment process as the only treatment process. In order to evaluate the cost and GHG generation in the developed hybrid treatment system, results of continuous operation on CTMP wastewater from the present work as well as results of study on CO_2 dissolution in CTMP wastewater (Kazemi, 2013) and other literature were used. In the developed hybrid treatment process, it is assumed that a spray scrubber is used only to increase the contact between liquid wastewater and the flue gas without using any alkaline solution. Accordingly, wastewater entering the anaerobic reactor is saturated with carbon dioxide that is a substrate for methanogenic bacteria and can be converted to CH_4. Anaerobic treatment is followed by aerobic treatment for additional COD removal. It is assumed that the saturation of wastewater with CO_2 does not have any effect on sludge production or aerobic treatment. The difference between the conventional hybrid process and the developed hybrid process with CO_2 saturated wastewater is in their costs and GHG emissions. It is assumed that the CO_2 stream would be introduced in the same manner for different anaerobic reactors (IC reactor applied at Matane treatment plant and UASB reactor applied in the present study) in a way that saturation of wastewater with CO_2 occurs in the scrubber prior to entering the anaerobic reactor.

The flow diagram of Tembec Matane WWTP is shown in Figure 5.2. The input and output sources of energy are shown. The GHG emissions are shown in red. Tembec Matane wastewater treatment process consists of a primary treatment in which most of large particles are physically removed from wastewater. After primary clarifier, the wastewater enters the biological treatment as a secondary treatment. The secondary treatment consists of an anaerobic internal circulator reactor (IC) which is followed by an aerobic activated sludge reactor. The information provided by the Tembec Matane CTMP WWTP is summarized in Table 5.1. More information is presented in Appendix B.

Table 5.1: Information provided by Tembec Matane WWTP.

	Anaerobic	Aerobic
Retention time	7 hours	
Capital cost	25 M ([1*]2012)	10M ([2*]1989)= 16.45M(2012)
Operational lifetime	30 years	50 years
Solid waste produced	230 m^3/month	12 dry tons /day=4380dry tons/year
Cost of solid waste treatment	Cash entry (100$/$m^3$)	
Treatment of solid wastes	Sold	Landfill
Recycling of wastewater	None	None
Recycling of gas	95% (to dry pulp)	[3*]NA
Recycling of solid waste	Sold	None
CH_4/kg COD removed	0.4 m^3/kg COD removed	NA
CH_4 % in biogas	70-75%	NA
COD removal	65%	85-90%
BOD removal	-	> 99%
Cost	-	12$/t of pulp produce
Gas collection from landfill	-	None (uncovered landfill)
Reactor type	IC (internal circulation)	Activated sludge

Additional information: The CTMP plant produces on average 25 m^3 of wastewater per ton of pulp with COD/BOD=2.13. The energy for the pulping plant is provided by using 2039 kWh electricity per ton of pulp as well as 0.5GJ/ ton of pulp from fossil fuel combustion.
The anaerobic treatment provides 6 to 8 million dollars saving in the consumption of fossil fuel and chemicals. The plant uses fossil fuel (light oil) to dry the pulp. The produced methane from anaerobic digestion replaces 6 million litres of light oil at pulp dryers. The anaerobic treatment is between the primary clarifier and the aerobic treatment. The plant does not collect gas from the landfill.
Flow, temperature, pH, TSS, COD and BOD entering the anaerobic digestion are respectively equal to:13585 m^3/d (almost 5×10^6 m^3/y), 35°C, 5.93, 246 mg/l (3342 kg/d), 10200 mg/l (143.6 ton/d) and 4800 mg/l (67.6 ton/d)

1*Annual index for 2012= 584.6 (Web 6)

2*Annual index for 1989= 355.4, (Brown, 2007)

3*NA=Not Applicable

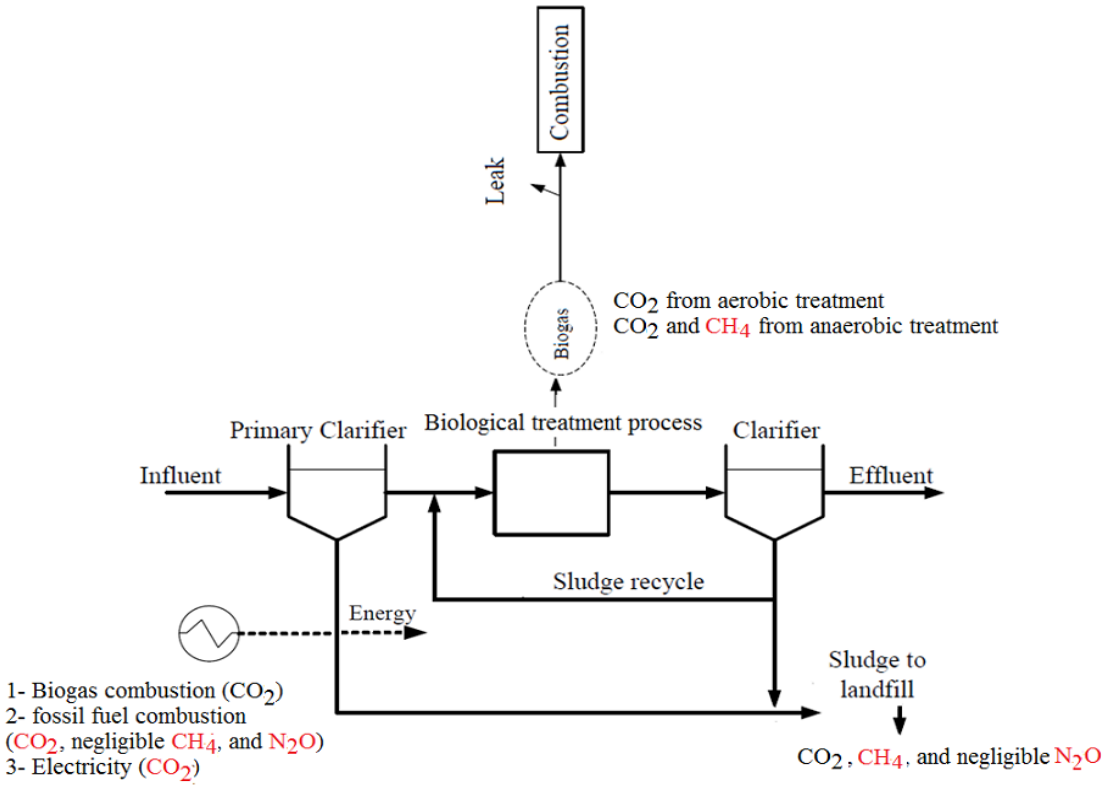


Fig 5.2: Flow diagram of the examined wastewater treatment system

In the following sections, cost estimation and GHG analysis would be done for the hybrid treatment (system A), aerobic (system B), and developed hybrid treatment (system C) processes. Table 5.2 shows the three different systems that were analyzed and compared based on their GHG emissions and costs. The anaerobic treatment alone was not considered as a treatment option because pulp and paper wastewater is usually a high strength wastewater and anaerobic treatment alone is not enough to remove organic matter to the required discharge standards.

Table 5.2: Treatment systems analyzed based on their GHG emission and cost.

Process design	Main treatment	Second treatment	Tertiary treatment	Nitrogen removal	Solid treatment	CO_2 injection
System A	Anaerobic	Aerobic	No	No	Landfilled	No
System B	Aerobic	No	No	No	Landfilled	No
System C	Anaerobic	Aerobic	No	No	Landfilled	Yes

Figure 5.3 shows the three treatment set ups that have been compared in the present work. The comparison is done based on the data provided by Tembec Matane WWTP and the review of literature.

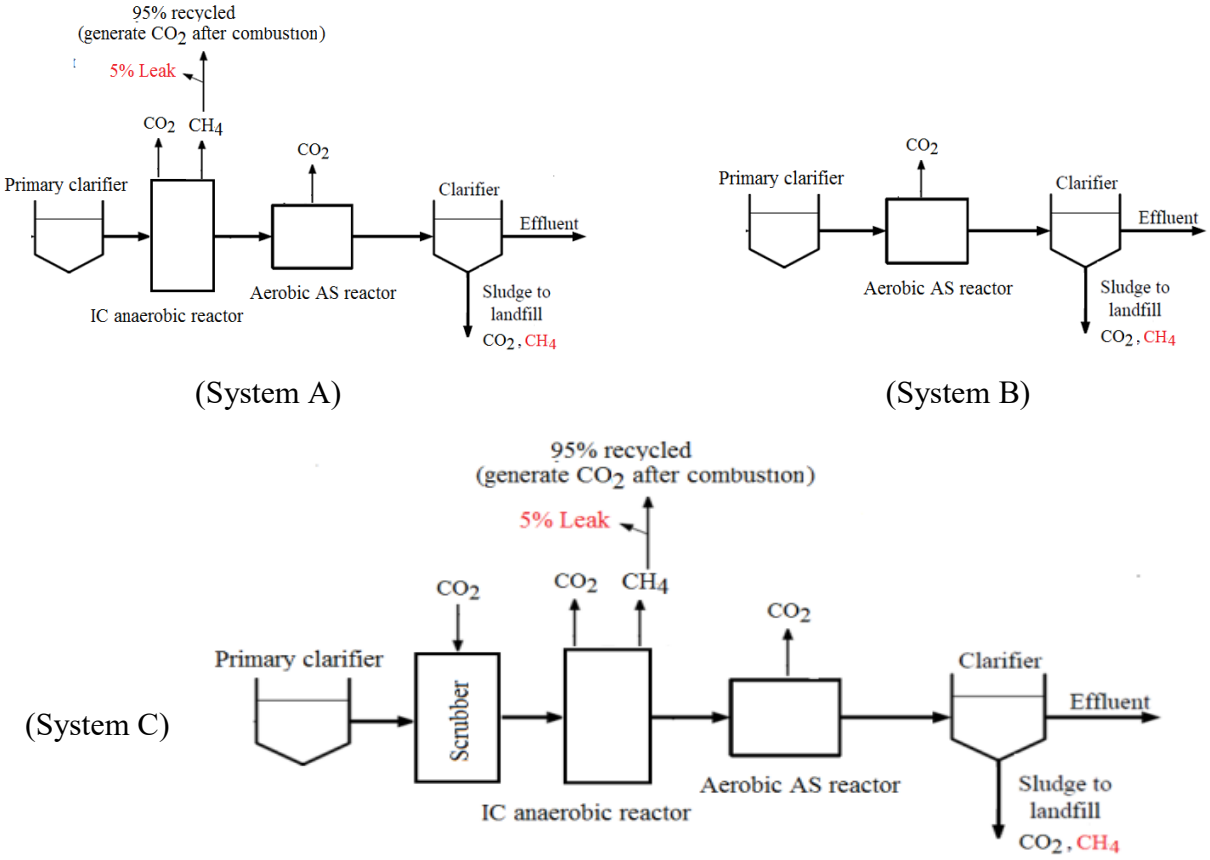


Fig. 5.3: Different treatment set up that have been compared in the present work

5.1 Assumptions

The assumptions made based on the literature review during the estimation of GHG emission and cost are presented in Table 5.3:

Table 5.3: List of assumptions

Off-site sources of GHG emissions are ignored to simplify the comparison.
For the estimation of GHG emission from landfills, a simplified first order decay approach is used, which is the default method recommended by the IPCC (IPCC, 2000a)
CO_2 production during power generation is assumed to be 0.96 kg CO_2/kWh (Cakir and Stenstrom, 2005; Keller and Hartley, 2003)
CO_2 production during biological treatment is assumed to be 1.19 g CO_2/g BOD removal (calculated based on information from Rittmann and McCarty, 2001 and Bani Shahabadi et al., 2010)
The growth yield coefficient of activated sludge is 0.5 kg dry activated sludge / kg removed BOD (Liu, 2003; Wei et al., 2003).
CO_2 content of the flue exhaust gas is equal to 60%
The only GHG emission reported from landfills belongs to CH_4. The generation of N_2O is negligible and CO_2 is part of the carbon cycle in nature (NCASI, 2005)
CO_2 emission from biological treatment is carbon neutral (not GHG) and N_2O emission is negligible
95% of biogas from anaerobic reactor is recovered (not GHG) and 5% leakage to the atmosphere (GHG)
CO_2 emission from the combustion of recovered methane is not considered as GHG
Energy requirement for biological treatment and scrubber operation in system A and C is provided by the combustion of recovered methane. Therefore the CO_2 generation from power

generation is not GHG.

Carbon offset sources:

- combustion of recovered methane and its use instead of fossil fuel as an energy source
- bioconversion of dissolved CO_2 (as a result of applying scrubber) to methane

The assumed costs and values:

- Carbon Credit (CC): U.S. $ 6.50 / ton CO_2e (Topo Geo, 2012).
- Light crude oil: 42$/bbl (0.26$/l)(Web 7)
- Electricity generation: 0.125$/kWh (Hydro Quebec, 2013)
- Sludge disposal: 17$/$m^3$ (Buyukkamaci and Koken, 2010)

5.2 GHG generation

In order to calculate GHG emissions by the Tembec Matane WWTP, only on-site sources are considered. These sources include: GHG emissions from biological treatment, energy production and sludge treatment. In the following sections, the GHG emission from each of the above mentioned set ups is separately calculated. All calculations and details are available in Appendix B.

5.2.1 GHG generation from conventional hybrid treatment system (system A)

In this section GHG generations (from biological treatment of wastewater, sludge treatment, and energy production) for anaerobic and aerobic treatment in the hybrid treatment process as well as carbon offset by this process are evaluated.

5.2.1.1 Anaerobic reactor

5.2.1.1a Biological treatment of wastewater

In the studied plant, anaerobic treatment is carried out at 35°C in an IC reactor. The flow rate, temperature, COD and BOD of wastewater entering the anaerobic digestion are respectively

equal to 13585 m^3/d (4958525 m^3/y), 35°C, 10200 mg/l (143.6 ton/d) and 4800 mg/l (67.6 ton/d).

The generated biogas from the anaerobic reactor has 70-75% methane and 25-30% CO_2. It is considered that the emission of N_2O and other GHGs from the anaerobic reactor is negligible compared to CH_4 and CO_2. The CO_2 in biogas is CO_2 neutral and is not considered as a GHG. However, the value of this emission is reported separately (8,680 tCO_2/y). On the other hand, CH_4 generated during anaerobic treatment of wastewater is a GHG if it enters the atmosphere.

The studied WWTP is equipped with a methane collection system to collect biogas from the anaerobic treatment reactor (13,000,000 m^3 CH_4/y). Approximately 95% of the produced biogas from the anaerobic treatment (12.5 M m^3 CH_4/y equals to 173,146 tCO_2e/y) is collected and burnt to dry the wet pulp. The recycled methane from anaerobic treatment replaces 6 million liters of light oil at pulp dryers and therefore offsets the CO_2 emission from the combustion of light oil. Only 5% of CH_4 emission as a result of leaks (657000 m^3 CH_4/y, equal to 9113 tCO_2e/y) is considered during GHG calculations. The values for biogas recovery and leaks from the Tembec plant are in agreement with the reported values in the literature (Bani Shahabadi et al., 2009; Leilieveld et al., 2005; Ashrafi, 2012).

The biogas generation is 0.4 m^3 CH_4/(kg COD removed), which shows the high efficiency of the system in biogas production. The focus of this study is on the wastewater treatment plant and not on the pulp making plant. Therefore, in order to determine the effect of methane recovery, it is assumed that the energy from combustion of recycled methane is spent in the treatment plant for aerobic and anaerobic treatment. The excess energy can be used for pulp drying.

5.2.1.1b Sludge treatment

The amount of sludge produced in the anaerobic treatment processes is low compared to the amount produced in the aerobic treatment processes. Tembec Matane produces 230 m^3 sludge/month which is sold as a source of anaerobic biomass. Consequently, no GHG emission is considered for sludge treatment produced from anaerobic treatment.

5.2.1.1c Energy production

To calculate the GHG emission from energy production, first the source of energy for anaerobic treatment has to be determined. According to Keller and Hartley (2003), the overall power requirement for anaerobic treatment (mixing, pumps, etc.) is 0.01 kW/m^3 reactor volume which

results in 347,000 kWh/y (≈ 333 ton CO_2/y) for the anaerobic reactor in the present study. On the other hand, the recovery of biogas generated in anaerobic bioreactor and its combustion yields $1.15*10^8$ kWh/y (412 TJ/y). The energy from the combustion of recovered biogas covers the entire energy needs of anaerobic treatment. In addition, it can compensate some other energy needs in the plant. This shows the importance of biogas recovery in anaerobic treatment. CO_2 generated from the combustion of recovered methane (110,000 ton CO_2/y) is not considered as a GHG, therefore no GHG is generated for power generation in anaerobic treatment.

5.2.1.1d Carbon offset by anaerobic treatment

The source of carbon offset in anaerobic treatment is:

- From the combustion of recycled methane instead of fossil fuel as an energy source (23,045 tons CO_2e/y) (See Appendix B).

5.2.1.2 Aerobic reactor

5.2.1.2a Biological treatment

In aerobic treatment processes, the BOD of wastewater is incorporated into new biomass or is biologically oxidized to CO_2. A fraction of biomass can further be converted to carbon dioxide via endogenous respiration. The formula commonly used for dissolved substrate and biomass are $C_{10}H_{19}O_3N$ and $C_5H_7O_2N$, respectively (Rittmann, and McCarty, 2001; Bani Shahabadi et al., 2010). The equations for the aerobic carbonaceous BOD and biomass decay are as follow:

$$0.02C_{10}H_{19}O_3N + 0.01NH_4^+ + 0.01HCO_3^- + 0.1O_2 \rightarrow 0.03C_5H_7O_2N + 0.11H_2O + 0.06CO_2$$

$$0.05C_5H_7O_2N + 0.25O_2 \rightarrow 0.2CO_2 + 0.05NH_4^+ + 0.05HCO_3^- + 0.05H_2O$$

Therefore the total carbon dioxide emission from aerobic bioreactor would be the summation of CO_2 generation from biological oxidization of wastewater (0.66 g CO_2/g BOD_{rem}) and CO_2 generation from biomass conversion to CO_2 via endogenous respiration (0.53 g CO_2/g BOD_{rem}) and is equal to 1.19g CO_2/g BOD removal (0.66+0.53). For hybrid systems, if we assume 85% BOD removal in the anaerobic reactor and 15% BOD removal in aerobic reactor, therefore 4.4×10^9 gCO_2/y emission from aerobic bioreactor is expected as calculated in Appendix B. It

should be noted that CO_2 emission from aerobic reactors is not considered as a GHG because it originates from natural organic matter and biomass and is carbon neutral.

5.2.1.2b Sludge treatment

The aerobic treatment of wastewater produces a great amount of solid waste. In the studied plant, the generated waste (4380 dry tones/y) is sent to a landfill with no gas collection. Therefore, the generated gases are released to the atmosphere. Based on our assumptions, the only GHG emission reported from landfills belongs to CH_4. By applying first order decay approach of IPCC after a series of calculations, methane release to the atmosphere is estimated to be 306,242 m^3 CH_4/y which is equal to 4,245 tCO_2e/y. The details and calculations are presented in Appendix B.

If the landfill was equipped with a gas collection system and the generated methane from the landfill was collected, this CH_4 could be used as a source of energy to produce approximately 10TJ energy and save $350902 per year as calculated in Appendix B. On the other hand, this collection of methane could offset 564.92 ton CO_2e/y and produce 10.106 TJ/y energy, as calculated in Appendix B.

5.2.1.2c Energy generation

By assuming hybrid treatment of wastewater with 65% and 20% COD removal in anaerobic and aerobic treatment processes, respectively, the power required for aerobic treatment is equal to 15,173,000 kWh/y as presented in Appendix B. By assuming 0.96 kg CO_2 production/kWh, the CO_2 production from power generation for aerobic treatment in a hybrid treatment process is equal to 14,566 tCO_2/y. Table 5.4 shows the summary of the GHG generation from hybrid treatment system (system 1). In this table the GHG emissions are showed in red. Other emissions are also reported, however they are not considered as GHG emissions.

In summary power generated from the combustion of recovered methane is equal to 115 million kWh/y. The total power required for anaerobic and aerobic treatment is approximately equal to 15.5 million kWh/y (333,213+14,566,163) kg CO_2/y. Therefore, the combustion of recovered methane can provide the required power for the hybrid treatment plant. The excess power is approximately equal to 99 million kWh/y which can be used for the pulping process.

Table 5.4: Summary of the results of GHG emission for hybrid treatment system (system A).

		Biological treatment of WW	Sludge treatment	Energy generation	Carbon offset
Hybrid treatment system (system A)	Anaerobic treatment	CO_2:8,680 tCO_2/y 95% CH_4 recycled (173,150 tCO_2e/y) 5% CH_4 leakage (9,113 tCO_2e/y) N_2O: negligible	Sludge is sold (No GHG)	333 tCO_2/y generated from combustion of a portion of the recycled methane *	23,045 tCO_2e/y
	Aerobic treatment	4400 tCO_2/y	306,250 m^3CH_4/y (=4,250 tCO_2e/y)	14,600 tCO_2/y generated from combustion of a portion of the recycled methane	No
	Total	28,010 tCO_2e/y (Not GHG) 13,360 tCO_2e/y (GHG) 23,045 tCO_2e/y (carbon offset)			

*110,000 tCO_2/y generated from combustion of total recycled methane

5.2.2 GHG generation from the system with aerobic treatment as the only treatment process (system B):

In this section GHG generations (from biological treatment of wastewater, sludge treatment, and energy production) for aerobic treatment as the only treatment process as well as carbon offset by this process are evaluated.

5.2.2.1 Biological treatment

If the only treatment system is aerobic treatment with 95% BOD removal efficiency, the CO_2 emission from the aerobic reactor would be 2.79×10^7 kg CO_2/y as calculated in Appendix B.

5.2.2.2 Sludge treatment

If the only treatment method is aerobic treatment, then the solid biomass production would be equal to 11720 ton dry AS/y (63% more than hybrid treatment process). This calculation is based on the assumption that the growth yield coefficient of activated sludge is 0.5 which means that each kg of removed BOD produces 0.5 kg of dry activated sludge (Liu, 2003; Wei et al., 2003). Moreover, the BOD removal efficiency is considered to be 95% by using only aerobic treatment.

Methane generation from the studied landfill, if the only treatment method is aerobic treatment, would be equal to 910,656 m^3/y as calculated in Appendix B. Under this condition, by considering 10% reduction in the release of methane due to aerobic oxidation, the amount of methane released to the atmosphere from the landfill would be equal to 819590 m^3/y (equals to 11,359 tCO_2e/y). This value for hybrid system is equal to 306242 m^3/y, implying 513348 m^3/y reduction in methane generation (63% less GHG emission).

If the generated methane from the landfill was recovered and used as an energy source, it could produce approximately 27 TJ/y energy compared to energy generation by the hybrid system which equals 10.1 TJ/y, as presented in Appendix B.

The combustion of captured methane from the landfill, replacing fossil fuels, will offset 1512 ton CO_2/y emission and will result in savings of 939097$/y in electricity consumption, knowing that the CO_2 generated as a result of combustion of the collected methane from landfill is not a GHG.

5.2.2.3 Energy production:

If the overall power requirement for aerobic treatment is assumed to be 1.5 kWh/ kg COD_{rem} (Keller and Hartley, 2003) and the only treatment is aerobic treatment with 80% COD removal efficiency, then the power required for aerobic treatment would be 60692346kWh/y as presented in Appendix B.

If CO_2 production during power generation is assumed to be 0.96 kg CO_2/kWh (Cakir and Stenstrom, 2005; Keller and Hartley, 2003), then CO_2 production from power generation in aerobic treatment would be 58264652 kg CO_2/y. Table 5.5 shows the summary of the GHG generation from anaerobic treatment as the only treatment system (system B). In this table the GHG emissions are shown in red and non GHG emissions are reported in black.

Table 5.5: Summary of the results of GHG emission for aerobic treatment system (system B).

	Biological treatment of WW	Sludge treatment	Energy generation	Carbon offset
Aerobic treatment	27900 tCO_2/y (Not GHG)	11359 tCO_2e/y (GHG)	58265 tCO_2/y(GHG)	**No**
	69624 tCO_2e/y (GHG) 27900 tCO_2e/y (Not GHG)			

5.2.3 GHG generation from developed hybrid treatment system (system C)

In this section the GHG generations from the developed hybrid treatment system (system C) are evaluated based on the GHG emission from conventional hybrid treatment system (system A). The GHG emission from the developed process is assumed to be the summation of GHG emission from conventional hybrid treatment system (system A) and emissions/offsets by applying the scrubber. Therefore in this section, the effect of applying a scrubber on GHG emission will be evaluated and then these values will be added to the values from system A in order to find the emissions from system C.

CO_2 emission from Tembec Matane CTMP plant:

The required energy for Tembec Matane CTMP plant originates from two sources:

- Electricity : 2039 kwh per ton of pulp (7.3 GJ/ton of pulp)
- Fossil fuel: 0.5 GJ/t of pulp (139kWh/ton of pulp)

These results in 247 million m^3 CO_2/y emission from total energy generation processes for the plant (details are available in Appendix B). In this case study, the off-site sources of GHG emissions such as emission from electricity generation section were ignored. However, in order to have a reliable estimation of the ensuing emissions, it is assumed that electricity is generated inside the plant and therefore it contributes in CO_2 emission calculations.

5.2.3.1 Applying a scrubber: CO_2 quenching, power requirement

In this project, it is assumed that the generated CO_2 in the pulp-producing plant is dissolved in the stream of wastewater by applying a spray scrubber, followed by using anaerobic treatment to

biologically convert the dissolved CO_2 to CH_4 as a biogas to replace fossil fuels. In order to determine how much CO_2 could be dissolved in wastewater by using a scrubber, the annual amount of gas passing through the scrubber is calculated. Then the required liquid (wastewater) that should be in contact with the mentioned gas in the scrubber will be calculated. Finally, based on the capacity of wastewater for dissolving CO_2, the dissolved CO_2 in the wastewater passing through the scrubber will be calculated. The excess dissolved $CO_{2,}$ resulting from the use of scrubber, could later be converted to methane in an anaerobic reactor. Based on the results of continuous operation of reactors in the present work, it is assumed that almost 83 to 97% of the excess $CO_{2\ (aq)}$ that dissolves in the wastewater by applying a scrubber (compared to the control that has only some $CO_{2\ (aq)}$), is converted to methane. 95% of the converted methane can be recovered and 5% will leak and is considered as GHG. The details are presented in Appendix B and the summary is provided in Table 5.6. Numbers in this table are rounded.

Table 5.6: Summary of the results of applying the spray scrubber in system C.

Feature	Value
CO_2 content of flue exhaust	60%
Total gas passes through the scrubber	27,677 ft^3gas/min (cfm)
Total wastewater passes through the scrubber	14.5 to 291 million gal WW/y
Required power for the scrubber	20,639 watt/y
Required energy for scrubber	180,795 kWh/y
Cost of energy generation for scrubber operation	22,600 $/y
CO_2 emission from energy generation for the scrubber (not GHG)	174 tCO_2/y
CO_2 dissolved in the wastewater by applying the scrubber (carbon offset)	496 to 9,912 tCO_2/y
Carbon credit for the carbon offset by applying a scrubber	3,220 to 64,430 $/y
Excess methane generation from anaerobic reactor as a result of applying a scrubber	273,000 to 5,461,000 m^3 CH_4/y
Increase in methane generation in developed system compared to conventional Hybrid treatment system	From 2 to 41%
5% of excess methane generation from anaerobic reactor leaks (GHG)	13,650 to 273,000 m^3 (189 to 3785 tCO_2e/y)
95% of excess methane generation from anaerobic reactor recovered (not GHG)	259,400 to 5,188,000 m^3 additional CH_4 recovery (3,600 to 71,900 tCO_2e/y)
Energy equivalent of the excess recycled methane combustion	8.6 to 171 TJ/y (2.4 to 47.5 million kWh/y)
CO_2 emission from combustion of the Excess recovered CH_4	$2{,}283\ to\ 45{,}655\ tCO_2/y$
Savings in light oil fuel consumption by combustion of excess recovered methane from anaerobic reactor	244,386 to 4,887,715 L oil/y (63,540 to 1.27 M$/y)

5.2.3.2 Overall GHG generation from developed treatment system (system C)

As mentioned earlier, the overall GHG emission from system C is the summation of emissions from system A and emissions/offsets from applying the scrubber. Table 5.7 presents these values for system A, application of scrubber and system C. The details are presented in Appendix B. It should be noted that in the treatment systems A and C, the required energy for anaerobic treatment, aerobic treatment and scrubber operation is provided from the combustion of the

recovered methane from the anaerobic reactor. Therefore, the CO_2 generation from power generation is considered as carbon neutral.

Table 5.7 Summary of GHG generation and energy consumption for system A, application of scrubbers, and system C.

	System A	Applying scrubber	System C
CH_4 generation in anaerobic reactor (m^3 CH_4/y)	13,150,000	273,000 to 5,500,000	13,423,000 to 18,650,000
5% CH_4 leakage from the anaerobic reactor (GHG) (tCO_2e/y)	9113	189 to 3785	9,300 to 12,900
95% CH_4 recovery from the anaerobic reactor (m^3 CH_4/y)	12,500,000 (173,150 tCO_2e/y)	259,400 to 5,188,000 (3,600 to 71,900 tCO_2e/y)	176,740 to 245,000 tCO_2e/y
Energy equivalent of recycled methane combustion (kWh/y)	$1.15*10^8$	2.4 to $47.5 * 10^6$	1.17 to $1.62*10^8$
CO_2 emission from combustion of the recovered CH_4 (tCO_2/y)	110,000	2,280 *to* 45,655	112,680 to 156,000
Savings in light oil by combustion of recovered methane (l oil/y)	11.8×10^6	0.24 to 4.9×10^6	12 to 16.7×10^6
Revenue of saved light oil (M$/y)	3.1	0.06 to 1.3	3.1-4.3
Carbon offset (tCO_2e/y)	23,045	496 to 9,912	29,365 to 49,940
Carbon credit ($/y)	0.15 M	3,220 to 64,430	0.19 to 0.32 M
Energy required for power generation (kWh/y)	15.5M	180,800	15.68M
CO_2 emission from energy generation (tCO_2/y)	14,933	174	15107

5.2.3.3 Carbon offset in the developed process

There are two sources for carbon offset in developed process:

- From the bioconversion of dissolved CO_2 to methane (496 to 9,910 tCO_2/y).
- From the combustion of recovered methane and its use as an energy source, replacing fossil fuels (28,870 to 40,030 tCO_2e/y).

The total carbon offset from developed system therefore would be the summation of CO_2 offsets from two mentioned sources with the value of 29365 to 49940 tCO_2e/y. Then by assuming the

carbon credit to be 6.5$/t CO_2e, the carbon credit related to this carbon offset for the plant in the developed method will be 190,872 to 324,610 $/y (Details are presented in Appendix B).

Table 5.8 summarizes the emissions from biological treatment (both aerobic and anaerobic reactors), sludge treatment and energy generation for the developed hybrid treatment system (system C). It should be noted that in this treatment system, the required energy for anaerobic treatment, aerobic treatment and scrubber operation is provided from combustion of the recovered methane from anaerobic reactor. Therefore the CO_2 generation from power generation is considered as carbon neutral. The application of scrubber in the developed process is assumed to have no effect on the aerobic digestion, solid waste production or CO_2 emission from the anaerobic reactor.

Table 5.8: Summary of emissions from hybrid treatment system (system C).

		Biological treatment of WW	**Sludge treatment**	**Energy generation**	**Carbon offset**
Hybrid treatment system	**Anaerobic treatment**	CO_2:8,680 tCO_2/y 95% CH_4 recycled (176,740 to 245,000 tCO_2e/y) 5% CH_4 leakage (9,300 to 12,900 tCO_2e/y) N_2O: negligible	Sludge is sold (No GHG)	507 tCO_2/y	29,365 to 49,940 tCO_2e/y
	Aerobic treatment	4400 tCO_2/y	306,250 m^3CH_4/y (=4,250 tCO_2e/y)	14,600 tCO_2/y	**No**
	Total	28,190 tCO_2e/y (Not GHG) 13,550 to 17150 tCO_2e/y (GHG) 29,365 to 49,940 tCO_2e/y (carbon offset)			

The GHG emissions and energy requirements corresponding to the three treatment systems in the present work are summarized in Table 5.9, where GHG emissions are shown in red.

Table 5.9: Summary of GHG generation and energy consumption for systems A, B, and C

	System A	System B	System C
Energy requirement (M kWh/y)	15.5	60.7	15.7
CO_2 emission from energy generation (tCO_2/y)	14,933	58,265	15,107
CH_4 generation in anaerobic reactor (Mm^3 CH_4/y)	13.2	-	13.4 to 18.7
5% CH_4 leakage from the anaerobic reactor (tCO_2e/y)	9113	-	9,300 to 12,900
95% CH_4 recovery from the anaerobic reactor (tCO_2e/y)	173,150	-	176,740 to 245,000
Energy equivalent of recovered methane combustion (M kWh/y)	115	-	117 to 162
Saving in light oil by combustion of recovered methane (M l oil/y)	11.8	-	12 to 16.7
Revenue of saved light oil by methane recovery (M$/y)	3.1	-	3.1-4.3
CO_2 emission from combustion of the recovered CH_4 (tCO_2/y)	110,000	-	112,680 to 156,000
CO_2 emission from anaerobic reactor (tCO_2/y)	8,680	-	8,680
CH_4 emission from landfilling of aerobic reactor sludge (tCO_2e/y)	4,250	11,359	4,250
CO_2 emission from aerobic reactor (tCO_2/y)	4,400	27,900	4,400
Carbon credit (M$/y)	0.15	0	0.19 to 0.32
Carbon offset (tCO_2e/y)	23,045	0	29,365 to 49,940
Total GHG emission (tCO_2e/y)	13,360	69624	13,550 to 17,150
Total not GHG emissions (tCO_2e/y)	28,010	27,900	28,190

5.3 Cost analysis:

In this section, the costs and revenues to the plant from each of the three systems presented in Table 5.2 are evaluated.

5.3.1 Cost analysis for conventional hybrid treatment system (system A):

The costs of biological treatment of wastewater, sludge treatment, and energy production for the anaerobic and aerobic treatment in the hybrid treatment process as well as revenue from carbon offset, biogas generation, and selling sludge are evaluated in this section.

5.3.1.1 Anaerobic reactor

5.3.1.1a Biological treatment of wastewater:

Considering the price of light crude oil to be 0.26$/l (Web 3), saving approximately 11.8 million litres of light oil by the combustion of recovered methane from anaerobic treatment instead of light oil can bring 3.1 million dollar revenue per year for the plant. The information provided by the Tembec plant also shows that the methane recovery from anaerobic treatment corresponds to 6-8 million dollars in savings, as reported in this work.

5.3.1.1b Sludge treatment:

The solid waste produced from the anaerobic treatment in the examined treatment plant is sold for use in another plant. The cash entry to the company from selling this solid waste equals 100$/$m^3$ solid waste. Considering 230 m^3/month production of solid waste from anaerobic digestion, the total cash entry would be 276000$/y.

5.3.1.1c Energy production:

Anaerobic treatment requires energy for mixing, pumps, and other devices. The overall power required by anaerobic treatment was calculated to be 347097 kWh/y. By assuming 0.125$/kWh, the cost of power generation for anaerobic treatment would be 43387$/y.

5.3.1.1d Carbon Offset:

The total carbon offset by anaerobic treatment was calculated to be equal to 23,045 tons CO_2e/y. By applying the value of carbon credit (CC) which is U.S. $ 6.50 / ton CO_2e, the carbon offset by anaerobic treatment can bring revenue equal to 0.15 M$/y for the treatment plant.

5.3.1.2 Aerobic reactor

5.3.1.2a Sludge treatment:

Aerobic treatment of wastewater produces a large amount of sludge that is send to the landfill. Assuming paper-mill sludge with a dry bulk density of 250 $kg.m^{-3}$ and approximately 70% water content (Amini et al., 2012), and considering the cost of sludge disposal to be 17$/$m^3$ (Buyukkamaci and Koken, 2010), then the cost of sludge disposal to the landfill would be approximately 297840$/y. The calculation is presented in Appendix B.

5.3.1.2b Energy production and aerobic treatment:

Aerobic treatment requires energy for aeration, mixing, pumps, and other devices. The overall power required by aerobic treatment in the conventional hybrid process was calculated to be15173086.5kWh/y. If we assume 0.125$/kWh, the cost of aerobic treatment would be 1896636 $/y.

5.3.2 Cost analysis for aerobic treatment as the only treatment process (system B):

In this section the costs of biological treatment of wastewater, sludge treatment, and energy production for the aerobic treatment as the only treatment process are evaluated.

5.3.2.1 sludge treatment:

If aerobic treatment was the only treatment for the wastewater, then the amount of solid waste sent to the landfill would be equal to 11720 dry ton/y. Therefore, the cost of sludge disposal for this amount of solid waste would be 796960 $/year as shown in Appendix B.

5.3.2.2 Energy production and aerobic treatment:

Plants with aerobic treatment as the only method of treatment require 60692346 kWh power per year which costs 7586543$/y.

5.3.3 Cost analysis for developed hybrid treatment system (system C):

The costs of applying a developed treatment system (system C) is evaluated by adding the costs and revenues related to applying a scrubber with the costs of conventional hybrid treatment system (system A).

5.3.3.1 Costs of applying a scrubber:

The total cost of using the scrubber will be the summation of capital cost, operational and maintenance costs. These costs are estimated based on the values presented in Table 2.7, and the results are summarized in Table 5.10.

The operation costs decrease as the volume of processed gas increases. The maintenance cost, on the other hand, decreases based on the liquid type. If the liquid has very fine particles that do not clog the nozzles, the maintenance costs are much lower. In the Tembec Matane case study, the CTMP wastewater has very fine particles and a large amount of gas passes through the scrubber annually which decreases the operation and maintenance costs. It is not surprising that for applying the scrubber the maintenance cost is a considerable portion of the costs.

Table 5.10: Cost of applying a spray scrubber for the case study

Capital cost	276770$ ($10 per scfm)
Operation and maintenance cost	415155$ (22599$ assumed for operational cost, which leaves 392556$ for maintenance cost) ($15 per scfm), annually
Annualized cost	$424381 ($15.33 per scfm), annually
Life time	30 years (the same as anaerobic treatment life time)

The summary of the results of cost estimation for systems A, B and C is presented in Table 5.11.

Table 5.11: Summary of the cost analysis for system A, B and C.

		Biological treatment of WW	Sludge treatment	Energy generation	Carbon offset
Hybrid treatment system (system A)	**Anaerobic treatment**	Methane recovery saves 3.1 M$/y in light oil consumption	276,000$/y cash entry	43387$/y	0.15M$/y saving
	Aerobic treatment	see energy generation cost	297840$/y	1896636$/y	**No**
	Total	(3.5 M$/y revenue - 2.19 M$/y cost)= 1.3 M$ revenue			
Aerobic treatment (system B)		see energy generation cost	796960 $/year	7586543$/y.	**No**
	Total	8.4 M$/y cost			
Developed treatment system	**Anaerobic**	Methane recovery saves 3.1-4.3 M$/y in light oil consumption	276,000$/y cash entry	$ 467768	0.19 to 0.32 M$/y saving
	Aerobic treatment	see energy generation cost	297840$/y	1896636$/y	**No**
	Total	(3.6 to 4.9 M$/y revenue - 2.67 M$/y cost)= 0.93 to 2.23 M$ revenue			

Figure 5.4 presents the costs and revenues of the three treatment systems, which shows that despite the higher capital cost for hybrid treatment systems (system A and C) compared to the aerobic treatment process (system B), the total costs is lower. Moreover, considerable savings by

the combustion of recovered methane instead of fossil fuels is achieved in systems A and C. In system C, the carbon offset by applying a scrubber brings additional revenue compared to system A.

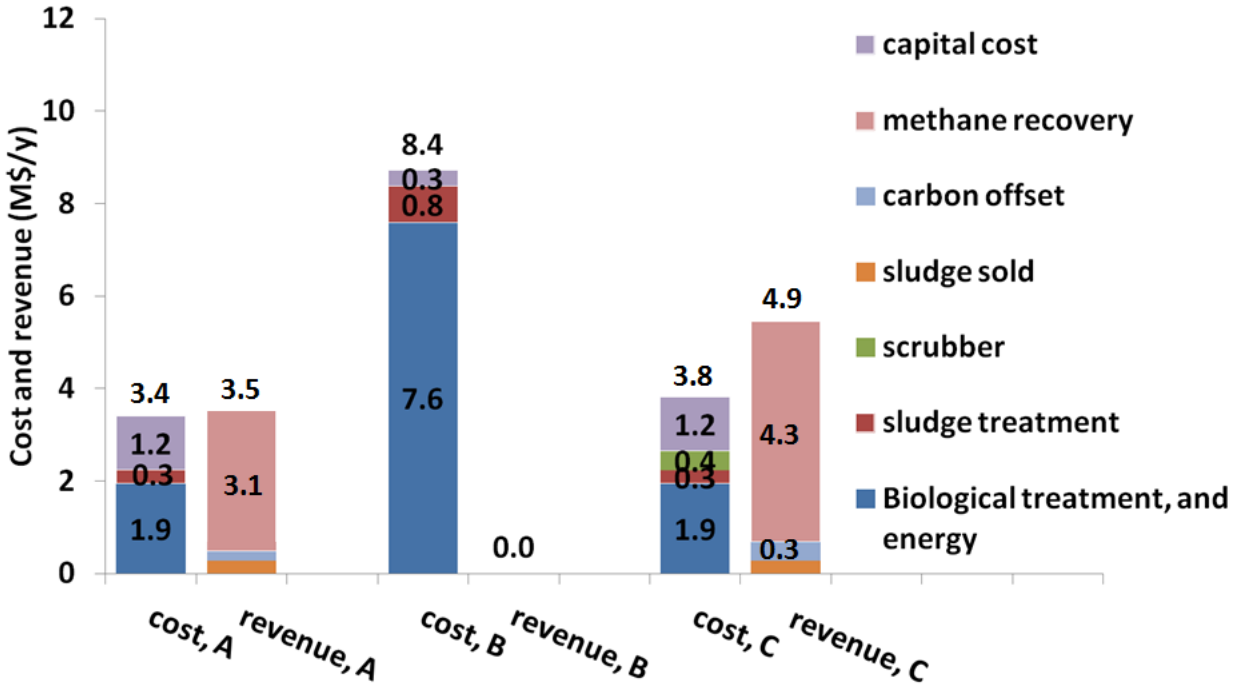


Fig. 5.4: Summary of cost analysis for systems A, B and C

5.4 GoldSET™ analysis

The GoldSET™ software, developed by Golder Associates to improve sustainability principles, was used to compare various treatment methods based on their corresponding economical, environmental and social aspects (GoldSET manual guide, 2011). The wastewater module for this software was developed by Concordia University.

"GoldSET is a multi-criteria decision analysis tool that integrates the environmental, social and economic dimensions of sustainable development (SD) into alternative analyses. The tool was specifically developed to embed sustainable development principles using a number of key indicators and variables into projects, and it can summarize interactions of sustainability analyses in easy-to-understand graphic formats" (GoldSET manual guide, 2011).

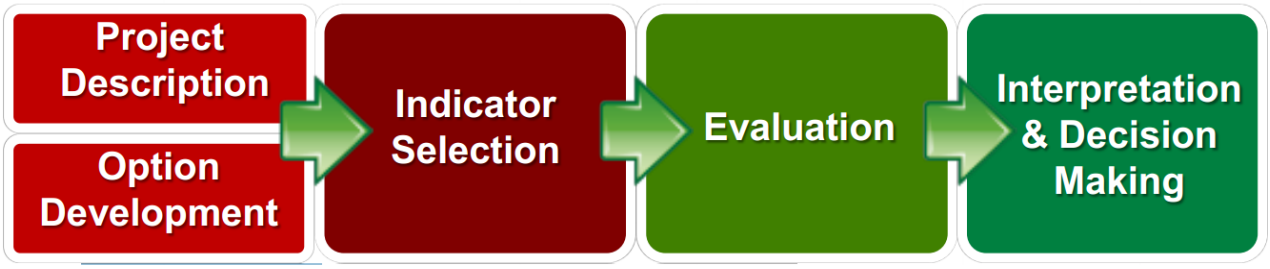


Fig. 5.5: GoldSET evaluation process (GoldSET manual guide 2011)

The GoldSET software has a 5-Step Evaluation Process as shown in Figure 5.5. They are:

1. Project Description: The project objectives are specified
2. Option development: Lists all scenarios that should be compared
3. Indicator Selection: Indicators are subjects that affect the overall performance of the project. A set of indicators are selected from the standard set of indicators in the software for wastewater treatment. An option is available to add or edit indicators according to project specificities. Selected indicators are then weighted to reflect their relative importance to the project.
4. Evaluation: Consists of qualitative and quantitative evaluation of the indicator which helps the ranking of options.
5. Interpretation & Decision Making: Performance of all options under consideration is compared graphically and numerically. In the results summary, a sustainability triangle is designed to show the performance in which each dimension shows one aspect of sustainability (Environmental, social, and economical dimensions). The most sustainable approach and the most suitable technology is the biggest and most balanced triangle with the highest performance in each dimension (GoldSET manual guide 2011; Chalise, 2014).

The summary of results obtained from the application of GoldSET software is presented in Figure 5.6. In this figure the three examined treatment systems (Table 5.2) are compared based on sustainability features (environmental, social, and economical features). For system C, there is a range of results based on liquid flow rates passing through the scrubber which is equal to 1 to 20 gal/1000 ft^3 gas passing through the scrubber. Consequently, the results are shown in two graphs related to the minimum and maximum numbers. Maximum numbers are achieved when higher liquid flow rates pass through the scrubber. From Figure 5.6, higher values and a higher balance of environmental, social, and economical aspects of sustainability belong to the

developed hybrid process (system C), indicating the high sustainability of this treatment method. Also, the results show the advantage of applying hybrid treatment over aerobic treatment for the treatment of CTMP pulp and paper wastewater. Figure 5.7 shows the strengths and weaknesses of each treatment process in different sustainability dimensions (environmental, economical, and social dimensions. The environmental dimension shows the weakness of aerobic treatment based on the high quantity of solid waste, GHG emission, no GHG offset, and no oil recovery. One the other hand, the developed hybrid process shows most of strengths in high GHG offset, and higher air quality, and lower GHG emission. From the social aspect, the hybrid developed process is strong in giving response to social sensitivity toward the reduction of GHG. The economical dimension shows that is the most costly method with a higher need for fuel and there is no biogas generation and recovery. On the other hand, the developed hybrid treatment process shows the highest strength between the three treatment processes and has highest carbon credit, and biogas recovery.

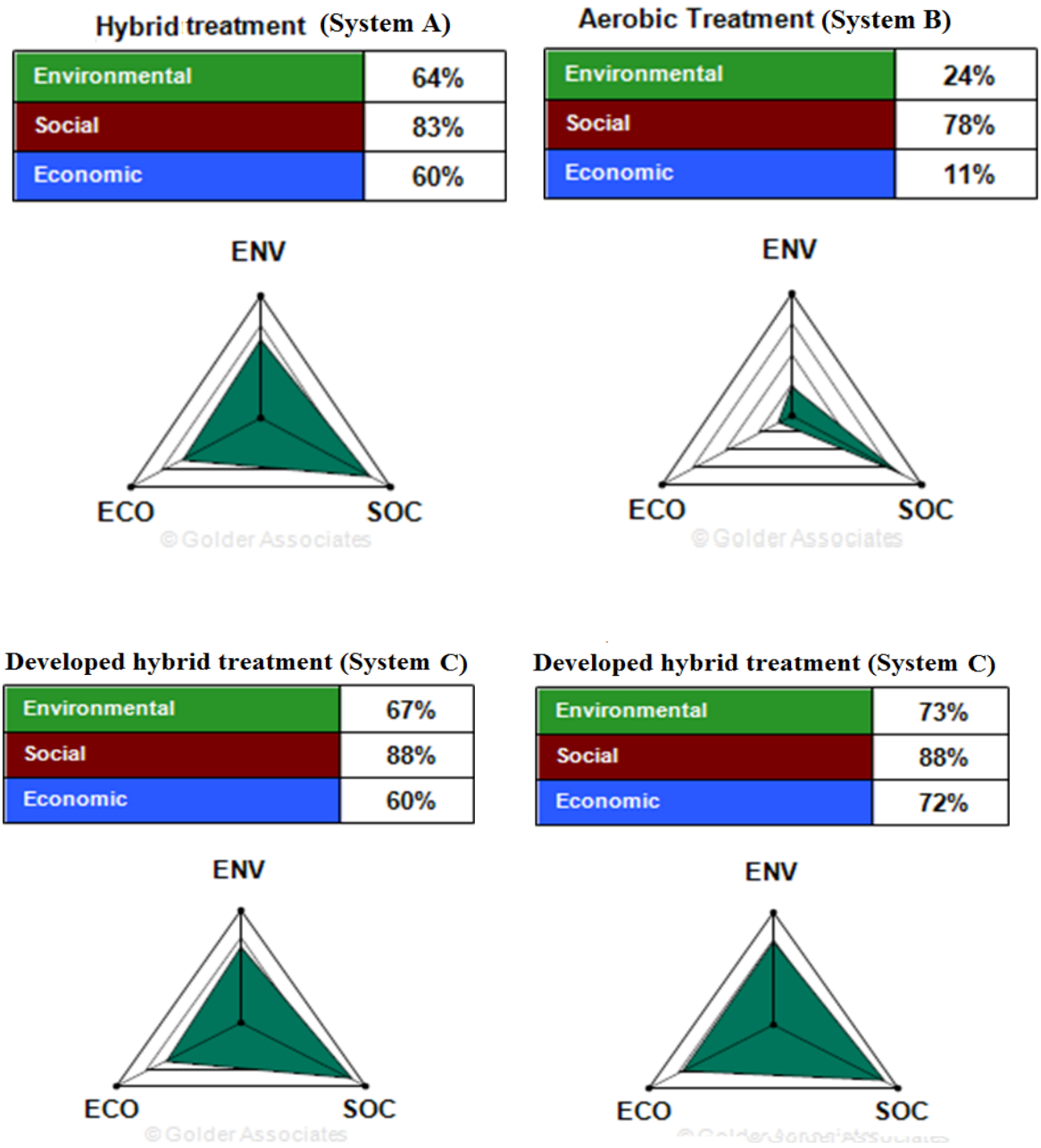
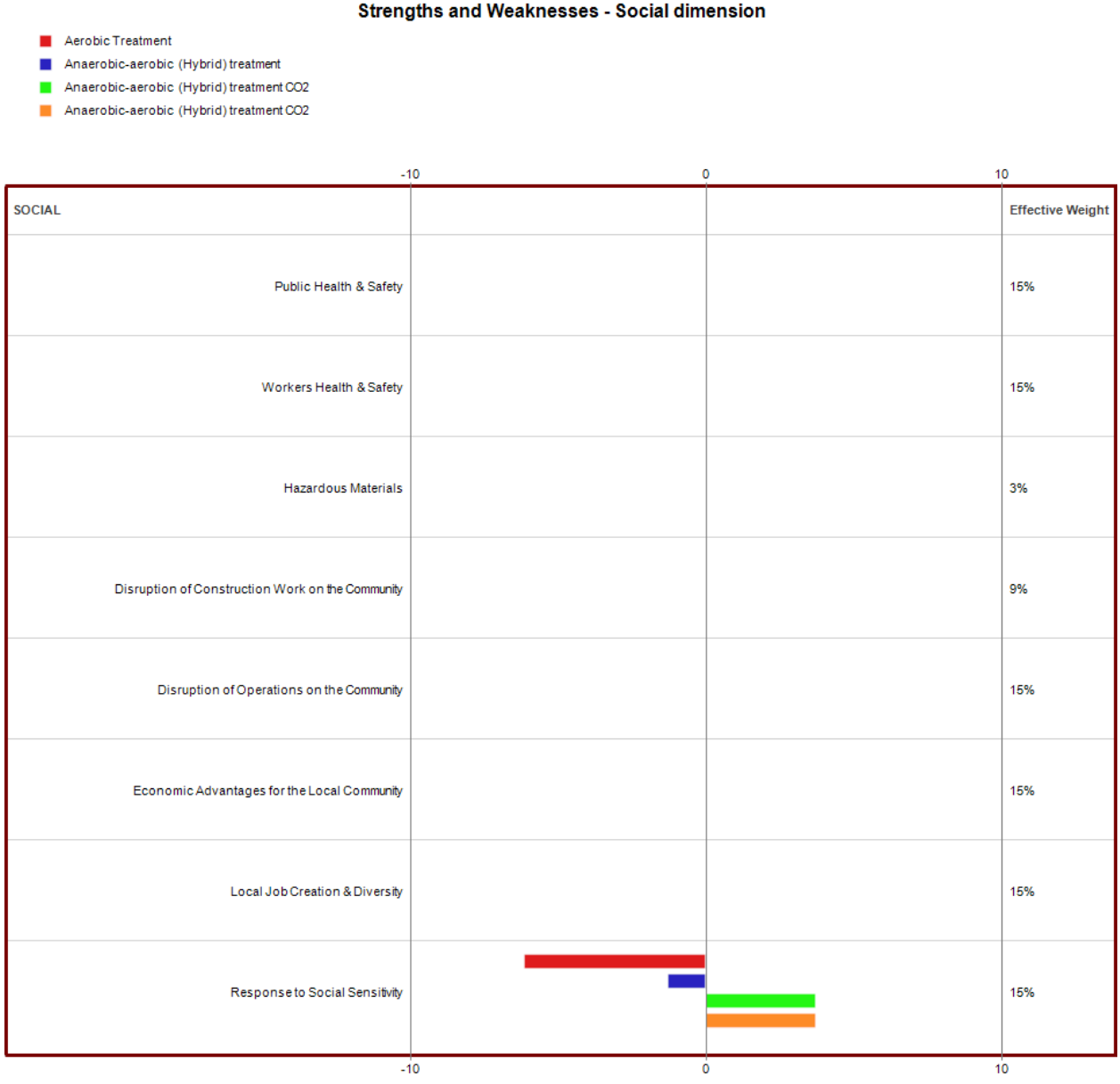


Fig. 5.6: Summary of the GoldSET software results


Strengths and Weaknesses - Environmental dimension
Aerobic Treatment
Anaerobic-aerobic (Hybrid) treatment
Anaerobic-aerobic (Hybrid) treatment CO2
Anaerobic-aerobic (Hybrid) treatment CO2
-10
0
10
ENVIRONMENTAL
Effective Weight
Quality of Solid Waste
4%
Quantity of Solid Output
10%
Solid Output Re-Use
10%
Greenhouse Gas Emissions
10%
Air Quality
8%
Green house gas offset
10%
Quality of Wastewater Discharge
10%
Liquid Output Re-Use
2%
Fuel / Oil Recovered
10%
Energy Consumption
10%
Impacts of Failure on Natural Environment
8%
Potential Impacts upon Ecological Integrity
8%
-10
0
10


Strengths and Weaknesses - Social dimension
Aerobic Treatment
Anaerobic-aerobic (Hybrid) treatment
Anaerobic-aerobic (Hybrid) treatment CO2
Anaerobic-aerobic (Hybrid) treatment CO2
-10
0
10
SOCIAL
Effective Weight
Public Health & Safety
15%
Workers Health & Safety
15%
Hazardous Materials
3%
Disruption of Construction Work on the Community
9%
Disruption of Operations on the Community
15%
Economic Advantages for the Local Community
15%
Local Job Creation & Diversity
15%
Response to Social Sensitivity
15%
-10
0
10

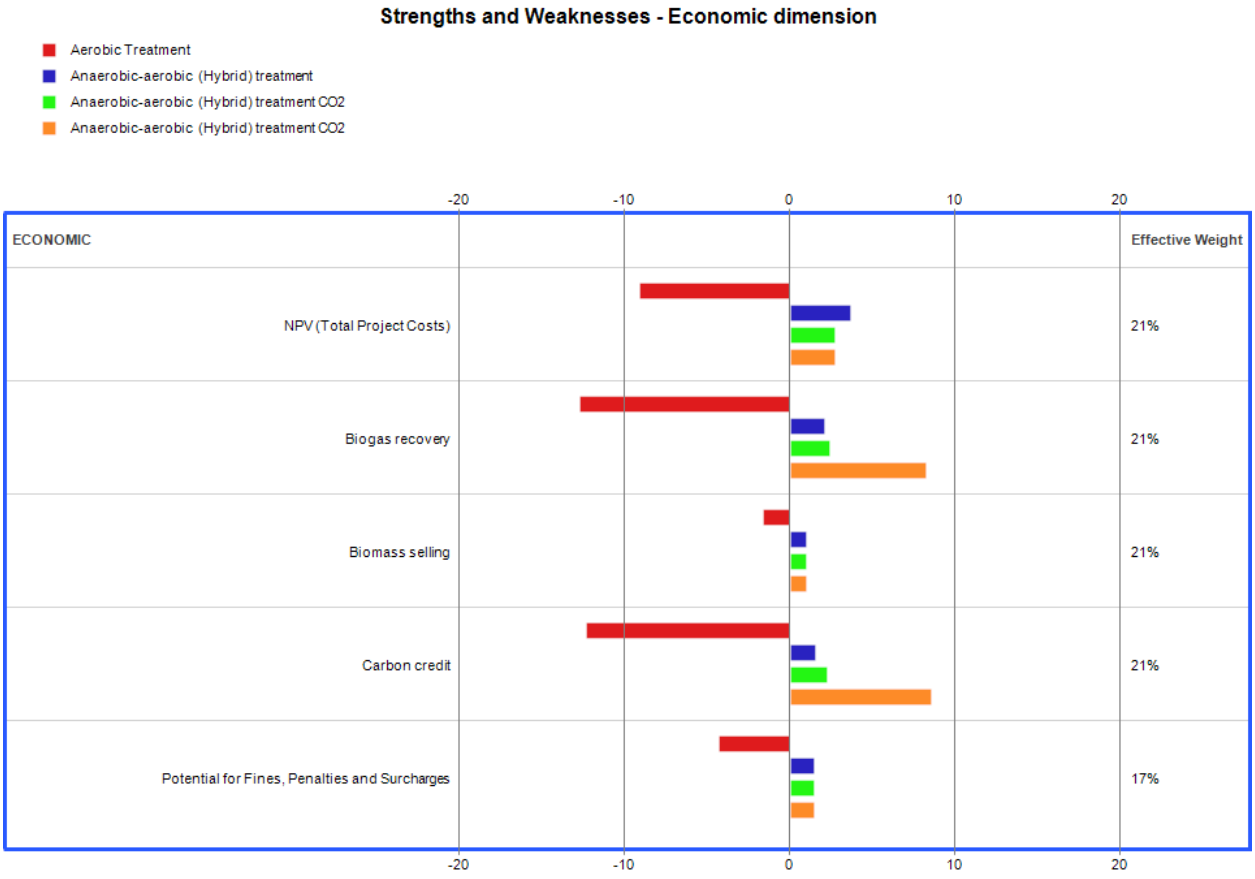


Fig. 5.7: GoldSET software output- results based on strengths and weaknesses of each process in different sustainability aspects.

Chapter 6: Conclusions

In the present work, an anaerobic process is developed for CO_2 bioconversion to methane during the treatment of wastewater. This conversion is based on the last step of anaerobic digestion in which anaerobic bacteria consume hydrogen and carbon dioxide to produce methane as a biogas. Two series of batch tests were performed followed by continuous experiments in one-stage anaerobic UASB reactors. Results of batch tests showed the feasibility of applying the developed process for CO_2 removal using the pulp and paper wastewater. Higher CO_2 removal was achieved in samples with lower pH, higher temperature and in the presence of CO_2 injection. Results showed that COD removal was almost constant in all operating conditions. The injection of CO_2, increased methane generation at all operating pH values. On the other hand, methane generation was higher at higher pH values which are more suitable for methanogenic activities. However, the increase in methane generation in the samples with CO_2 injection compared to the control samples was higher at lower pH values which resulted from higher dissolved CO_2 in the samples with lower pH, which could further be converted to methane.

The results of continuous experiments showed that by increasing the organic loading rate, methane production decreased in the reactor with CO_2 injection compared to the control reactor with no CO_2 injection. The reason for this observation is the lower pH of the influent in the reactor with CO_2 injection. The CO_2-saturated wastewater as the influent of the UASB reactor had a pH around 5.5 which is not a suitable pH for methanogenic activity, compared to the influent of the control reactor that had the pH around 6.5 that is a suitable pH for methanogenic activity. The effect of influent pH was eliminated by applying another continuous experiment in which the control reactor had the same influent pH as the reactor with CO_2 injection. Higher methane generation in the reactor with CO_2 injection compared to the control reactor with the same influent pH demonstrates the conversion of CO_2 to methane. The results also showed that the injection of carbon dioxide didn't make a considerable impact on COD removal efficiency.

By increasing the organic loading rate from 1 to 3 g COD/l.d, COD removal decreased by 5% because the contact time between wastewater and bacteria decreased.

In order to investigate the fate of CO_2, the fractions of CO_2 distributed in potential pathways were calculated. The results showed that under all operating conditions, in the reactor with CO_2 injection compared to the control reactor, higher CO_2 conversions to methane were observed. The observed CO_2 conversion corresponds to approximately 4000 mg CO_2/l in the reactor with CO_2 injection, compared to less than 2900 mg CO_2/l in the control reactor with the same influent pH. In experiments with CO_2 injection, approximately an additional 1400 mg/l CO_2 was dissolved compared to the control experiments with no CO_2 injection. Results showed that 83-97% of the excess dissolved carbon dioxide in samples with CO_2 injection compared to the control sample with the same pH, was participated in removal pathway and conversion to methane and it resulted because of the facility of consuming the dissolved CO_2 by the methanogenic bacteria. The proposed process in this work is very efficient for wastewaters with higher pH values and alkalinity that can dissolve more CO_2, which can be further converted into methane.

GHG emission and overall cost of a developed hybrid wastewater treatment system were compared with those of conventional aerobic and hybrid treatment processes. The developed hybrid wastewater treatment system uses a spray scrubber for the saturation of wastewater with CO_2 before entering the anaerobic reactor. The results showed the advantage of applying hybrid over aerobic treatment.

The addition of CO_2 in the developed hybrid treatment process (compared to the conventional hybrid treatment process) increases methane generation by 2 to 41 times, depending on the volume of wastewater in contact with the gas in the scrubber (These values respectively correspond to 1.34×10^{-4} to 2.7×10^{-3} m^3 liquid/m^3 gas (passing through the scrubber). The suggested process increases methane generation by 273057 to 5461145 m^3 CH_4/y compared to the conventional hybrid treatment process. The increase in methane generation yield will in turn increase the potential recovery of methane which will increase energy generation through its combustion, thus producing higher revenue for the plant. Power generation from the combustion of recovered methane in both conventional and hybrid treatment systems was more than the required power for the treatment process. Besides, CO_2 emission from the combustion of recovered methane for power generation is not considered as a GHG.

The annual cost and revenue of the developed hybrid treatment system was estimated to be 2.7 and 3.6 to 4.9 M$/y, while the corresponding values for the conventional hybrid treatment system was equal to 2.2 and 3.5M$/y. Aerobic treatment, on the other hand brings no revenue for the treatment plant and has 8.4M$/y cost for the treatment plant. The approximate GHG offset by the developed hybrid treatment, conventional hybrid treatment and aerobic treatment process respectively was equal to 29365 to 49940, 23045 and zero tCO_2e/y. By comparing the conventional hybrid treatment system with the developed hybrid process with respect to GHG emission and cost, it can be concluded that applying a scrubber for the saturation of wastewater with CO_2 is a promising method, especially when higher liquid flow rates can pass through the scrubber. It can annually save up to 1 million dollars in annual costs of treatment plants and will reduce GHG emissions by 27,000 tCO_2e/y. The results of GoldSET software confirmed the higher sustainability of the developed hybrid treatment process.

Chapter 7: Contribution to Knowledge & Recommendations for Future Work

Contribution to Knowledge

This study developed a novel method for CO_2 removal by applying anaerobic treatment of pulp and paper industry. A few studies are devoted to the reduction of carbon dioxide through anaerobic digestion of food and municipal waste (Fernandez et al.,2014; Salomoni et al., 2011; Sato and Ochi, 1994). However, only one research has been done on the feasibility of anaerobic treatment of wastewater for CO_2 reduction which used synthetic wastewater (Alimahmoodi et al., 2008). In this study the feasibility of conversion of CO_2 to methane and increase in methane generation yield by the injection of CO_2 to the paper wastewater was demonstrated both in batch tests and continuous experiments. In this work industrial paper wastewater was used, therefore the method can be implemented for a real case.

The developed method is very efficient in decreasing the GHG emission from the wastewater treatment plant and CO_2 removal. The application of a scrubber without applying a basic solution, increases the CO_2 dissolution in wastewater while it doesn't have the difficulty of regenerating the basic solution. This method is simple, feasible, and economical.

The effect of different operating conditions (pH, temperatures, OLR, and HRT) was investigated for the developed process. The effect of CO_2 injection on wastewater treatment and COD removal was investigated.

A comprehensive cost estimation and GHG analysis was made for the developed process based on the experimental data and the information from the wastewater treatment plant that was provider of CTMP wastewater for this project.

A comparison between the developed process and conventional hybrid and aerobic treatment processes was made based on cost estimation and GHG emissions from each treatment. GoldSET^{TM} software was applied to compare the three mentioned treatment processes based on different aspects of sustainability which are environmental, economical and social aspects. The

results showed the higher sustainability of the developed process compared to the conventional treatment methods.

Recommendations for Future Work

The results of this study have demonstrated the feasibility of CO_2 removal from industrial flue emission in a sustainable process. Wastewaters with higher pH and alkalinity have a higher potential for CO_2 dissolution. Therefore to continue this study and find out the maximum potential of CO_2 removal, it is recommended that the effect of CO_2 injection be evaluated by applying a wastewater with high pH and alkalinity. In order to increase CO_2 removal and methane generation, it is recommended to inject CO_2 less frequently, which avoids the pH drop associated with CO_2 injection and unfavorable pH for methanogenic activity.

In order to develop the proposed process in this study, a one-stage anaerobic treatment was applied. However, this process could be done in a two-stage anaerobic treatment process which enables the study of reactor configuration and the best time for CO_2 injection.

A mathematical model could be developed based on the experimental data and the results of kinetic study in this project in order to design an industrial scale.

No study have been reported the microbial community data in anaerobic reactor with CO_2 enrichment. Such study could be very useful in understanding of the mechanisms of CO_2 utilization.

References:

ABB Pulp and Paper report (2008), "Industrial IT for Papermaking; Energy savings: The profit opportunity is yours", (http://www02.abb.com/global/seitp/seitp202.nsf/99ad595c32e0c2d9c12566e1000a4540/06a02103120d7ecc125765400321969/$FILE/Energy%20savings%20P&P.pdf)

Abedi N., Jiang X., Mulligan C.N., Yerushalmi L. (2012), "Development of a sustainable method to reduce carbon dioxide emissions by bioconversion into methane", CSCE conference, Alberta June 6-9.

Aigner, Jacqeline L. Editor (2011), "Greenhouse Gas Emission Scenarios for Use in Climate Based Response", Nova Science Publishers, p205.

Alexandersson T., Malmqvist A. (2005), "Treatment of packaging board whitewater in anaerobic/aerobic biokidney.", Water Sci. Technol. 52,10: pp 289-298.

Alimahmoodi, M. (2009) ,"Treatment of Aqueous waste streams contaminated with carbon dioxide and crude oil from an enhanced oil recovery process", PhD thesis, Concordia University.

Alimahmoodi, M. and Mulligan, C. N. (2008), “Anaerobic bioconversion of carbon dioxide to biogas in an upflow anaerobic sludge blanket reactor”, J. Air Waste Management Association, 58: pp 95-103.

Amini S., Movahedi Naeini S.A.R. and Mashayekhi K. (2012), "Effects of Paper-Mill Sludge as a Mulch versus Topsoil Incorporation on Potassium Uptake and the Grain Yield of Rain-Fed Wheat in a High Specific Surface Loess Soil with Iolite Dominance in Clay Fraction", Hindawi Publishing Corporation, Applied and Environmental Soil Science, Article ID 624824, 10 pages, doi:10.1155/2012/624824

Anaerobic digestion model No.1 (ADM1), by IWA task group for mathematical modeling of anaerobic wastewater processes, (first published 2002).

Argelis A. M., A. (2007), “Co- conversion of gaseous carbon dioxide and a high strength aqueous organic contaminant (phenol) to methane via a UASB reactor”, M.ASc thesis, Concordia University.

Ashrafi O. (2012), "Estimation of greenhouse gas emissions in wastewater treatment plant of pulp and paper industry", PhD thesis, Department of building, civil and environmental engineering, Concordia University, CA.

Bani Shahabadi M., Yerushalmi L., Haghighat F. (2010), " Estimation of greenhouse gas generation in wastewater treatment plants – Model development and application"Chemosphere 78: pp1085-1092.

Bani Shahabadi M., Yerushalmi L., Haghighat F. (2009), "Impact of process design on greenhouse gas (GHG) generation by wastewater treatment plants." Water Research 43: pp 2679-2687.

Beers A., (2010), " Energy from wastewater How breweries can tap undiscovered energy resources ", Technology for water ENVIROCHEMIE

Belcher A. and Barbero R., Nanowork news (2010), http://www.nanowerk.com/news/newsid=18153.php

Boot-Handford M.E., Abanades J.C., Anthony E.J., Blunt M.J., Brandani S., Mac Dowell N., Fernandez J.R., Ferrari M.C., Gross R., Hallett J.P., Haszeldine R.S., Heptonstall P., Lyngfelt A., Makuch Z., Mangano E., Porter R.T.J., Pourkashanian M., Rochelle G.T., Shah N., Yaoa J.G., and Fennell P.S.; (2014), "Carbon capture and storage update", Energy Environ. Sci., 7, p130

Boysen E. and Muir N.C. (2011), “Convert Carbon Dioxide into Fuel with Nanotechnology” Nanotechnology For Dummies, 2nd Edition. http://www.dummies.com/how-to/content/convert-carbon-dioxide-into-fuel-with-nanotechnolo.html

Bridle T, Shaw A, Cooper S, Yap KC, Third K, Domurad M. (2008), "Estimation of greenhouse gas emissions from wastewater treatment plants" Proceedings IWA World Water Congress, Vienna (Austria).

Brown T. (2007), "Engineering Economics and Economic Design for Process Engineers", CRC press, Tailor and Francis group, p 283.

Buyukkamaci N., Koken E. (2010), "Economic evaluation of alternative wastewater treatment plant ons for pulp and paper industry" Science of the total Environment 408: pp 6070-6078.

Cakir F.Y., Stenstrom M.K. (2005), "Greenhouse gas production: a comparison between aerobic and anaerobic wastewater treatment technology", Water Research 39: pp 4197–4203.

Carlson D. and Lingl P. from David Suzuki foundation and Wong R. from Pembina institute (2009), "Purchasing carbon offsets: A guide for Canadian consumers, businesses, and organizations", Third revision.

Chalise, Anupama Regmi (2014), "Selection of sustainability indicators for wastewater treatment technologies", A thesis in the department of Building, Civil, and Environmental Engineering, Concordia University.

Chan Y.J., Chong M.F., Law C.L., Hassell D.G. (2009), " A review on anaerobic-aerobic treatment of industrial and municipal wastewater" Chemical engineering J.,155: pp 1-18.

Chen Y., Cheng J.J, Creamer K.S. (2008), " Inhibition of anaerobic digestion process: A review", Bioresource Technology 99: pp 4044–4064.

Chinn D., Vu D., Driver M., Boudreau L., (2005)," CO_2 removal from gas using ionic liquid absorbents", patent publication number: US20050129598 A1, available at https://www.google.com/patents/US20050129598?dq=patent+co2+removal+method&hl=en&sa=X&ved=0ahUKEwjdrtXdq-LJAhXG6RQKHcAeCa8Q6AEIHTAA

Chu J. (2012), “Hybrid copper-gold nanoparticles convert CO2 may reduce greenhouse gas emissions” MIT News Office, http://web.mit.edu/newsoffice/2012/hybrid-copper-gold-nanoparticles-convert-co2.html

Clesceri L. S., Greenberg A. E. and Eaton A. D. (1998), "Standard Methods for the Examination of Water and Wastewater, Published by the American Public Health Association", the American Water Works Association and the Water Environment Federation, New York.

Cohen G.N. (2011), "Microbial biochemistry"; second edition; New York, Springer: ch.13, Methanogens and Methylotrophs, pp 139-161.

Cooper C.D. and Alley F.C. (2011), "Air pollution control: A design approach." (4 ed.). Long Grove, IL: Waveland Press, Inc.

Cornacchio L.A.T. (1989), "Anaerobic treatability of pulp and paper effluent", MASc thesis, University of Guelph, ON, Canada.

Driessen W.J.B.M., Habets L.H.A, Zumbragel M. (1999), "Anaerobic treatment of recycled paper mill effluent with the internal circulation reactor.", In: 6th IAWQ Symposium on Forest Industry wastewaters, Tampere, Finland.

Ekstrand E.M., Larsson M., Truong X.B., Cardell L., Borgstrom Y., Björn A., Ejlertsson J., Bo Svensson, Nilsson F. and Karlsson A. (2013), "Methane potentials of the Swedish pulp and paper industry - A screening of wastewater effluents", Applied Energy, 112: pp 507-517

Elliot A., Mahmood T. (2007), "Pretreatment technologies for advancing anaerobic digestion of pulp and paper biotreatment residues", Water Research, 41: pp 4273-4286

Environment Canada (2012), “Greenhouse Gas Sources and Sinks in Canada”, National Inventory Report 1990–2010.

EPA (2002), "Air pollution control technology fact sheet". (http://www.epa.gov/ttn/catc/dir1/fventuri.pdf)

Fabry V.J., Seibel B.A., Feely R.A., and Orr J.C. (2008), “Impacts of ocean acidification on marine fauna and ecosystem processes.” ICES Journal of Marine Science, 65: pp 414–432.

Fernandez Y.B., Soares A., Villa R., Vale P. and Cartmell E. (2014), "Carbon capture and biogas enhancement by carbon dioxide enrichment of anaerobic digesters treating sewage sludge or food waste", Bioresource Technology 159: pp 1-7.

Fernandez Y.B., McAdam E., Soares A., and Cartmell E. (2012), "Improving anaerobic digestion by injecting carbon dioxide", Cranfield Water Science Institute, Sponsored by Severn Trent water, EPSRC and WRAP.

Flinders, C. (2009), Water Profile of the United States Forest Products Industry. NCASI Technical Bulletin No. 960, National Council for Air and Stream Improvement, Inc., Research Triangle Park, NC.

Frankin R.J. (2001), “Full-scale experiences with anaerobic treatment of industrial wastewater” Water Science and Technology: a Journal of the International Association on Water Pollution Research 44.8: pp 1-6.

Gaur A., Park J.W., Jang J.H., Maken S., Lee J., and Song H.J. (2009), “Characteristics of Alkaline Wastewater Neutralization for CO2 Capture from Landfill Gas (LFG)” Energy Fuels 23: pp 5467–5473.

Global Climate and Energy Project (GCEP) (2005), “An Assessment of Carbon Capture Technology and Research Opportunities” GCEP Energy Assessment Analysis, STANFORD UNIVERSITY.

Grady C.P.L., Daigger Jr.G.T., Lim H.C. (1999), "Biological wastewater treatment", 2nd eddition., revised and expanded, CRC Press.

Graham, T. (2009) “Burying carbon dioxide in underground saline aquifers: political folly or climate change fix?” For the program on water issues, Munk centre for international studies university of Toronto.

Habets L.H.A., de Vegt A.L. (1991), "Anaerobic treatment of bleached TMP and CTMP effluent in the Biopaq UASB system", Water Sci. Technol. 24(3/4), pp 331-345.

Hach EPA;http://www.hach.com/epa

Hach procedure manual, (2009)

Hach procedure manual, (2005)

Hadiyanto S., Rostika R.N. and Handayani N.A. (2012), "Biofixation of carbon dioxide by Chlamydomonas sp. in a tubular photobioreactor" Int. Journal of Renewable Energy Development 1: pp 10-14.

Hedderich R., and Whitman W.B. (2006), "Physiology and Biochemistry of the Methane-Producing Archaea" Prokaryotes 2, CHAPTER 1.34: pp 1050–1079.

Herzog H., Caldeira K., and Reilly J. (2003), "An issue of permanence: Assessing the effectiveness of temporary carbon storage", Climatic Change, 59: pp 293–310.

Hydro Quebec (2013), "Comparison of Electricity Prices in Major North American Cities.", http://www.hydroquebec.com/publications/en/comparison_prices/pdf/comp_2013_en.pdf)

IPCC (international panel on climate change) Fourth Assessment Report: Climate Change (2007).

IPCC (international panel on climate change), Summary for Policymakers Emissions Scenarios, (2000a).

Jacobson M.Z., Delucchi M.A. (2011), "Providing all global energy with wind, water, and solar power, Part I: Technologies, energy resources, quantities and areas of infrastructure, and materials" Energy Policy 39.3: pp 1154–1169.

Jantsch T.G., Angelidaki I., Schmidt J.E., Bra~na de Hvidsten B.E., Ahring B.K. (2002), "Anaerobic biodegradation of spent sulphite liquor in a UASB reactor" Bioresource Technology 84: pp 15–20.

Kampschreur M.J., Temmink H., Kleerebezem R., Jetten M.S.M., van Loosdrecht M.C.M. (2009), "Nitrous oxide emission during wastewater treatment", Water Research, 43: pp 4093-4103.

Latorre A., Mamqvist A., Lacorte S., Welander T., Barcelo D. (2007), "Evaluation of the treatment efficiencies of paper mill whitewaters in terms of organic composition and toxicity", Environ. Pollut. 147: pp 648-655.

Maat D.Z. (1990), "Anaerobic treatment of pulp and paper effluents", In: Tappi Proceedings Environmental Conference, pp 757-759.

Mermillod P., Habets L.H.A., Van Driel E.F., de Vegt A.L. (1992), "Compact anaerobic/aerobic wastewater treatment at the Minguet & Thomas recycled paper mill in France", Tappi J., 9: pp 177-180.

Meyer T., Edwards E.A. (2014), "Review of Anaerobic digestion of pulp and paper mill wastewater and sludge", Water Research, 65: pp 321-349.

National Council for Air and Stream Improvement, Inc. (NCASI) (2005), "Calculation tools for estimating greenhouse gas emissions from pulp and paper mills", vesion1.1.

National Ocean and Atmospheric Administration (NOAA), earth system research laboratory (2015), available at http://www.esrl.noaa.gov/gmd/ccgg/trends/weekly.html

Pachauri R.K. and Reisinger A. (eds.) (2007), “Contribution of working groups I, II and III to the fourth assessment report of the intergovernmental panel on climate change”; IPCC, Geneva, Switzerland, p. 104.

Paasschens C.W.M., Habets L.H.A., de Vegt A.L. (1991), "Anaerobic treatment of recycled paper mill effluent in the Netherlands.", Tappi J., 11: pp109-113.

Pokhrel D., Viraraghavan T. (2004), "Treatment of pulp and paper mill wastewater—a review", Science of the Total Environment, 333: pp 37– 58.

Statistics Canada, (2010), available at: https://www.neb-one.gc.ca/nrg/ntgrtd/mrkt/archive/2010ndstrlnrgscnd/ndstrlnrgscnd-eng.html

US EPA (2014), available at http://www.epa.gov/climatechange/ghgemissions/gases/co2.html

Katsuyoshi T., Kaken Inc. (2008), (qtd. In Carbon Dioxide Reduction Technologies: A Synopsis of the Symposium at TMS 2008, Neale R. Neelameggham, JOM 60, 2: pp 36-41.

Kazemi, H. (2013), "The capacity of industrial pulp-and-paper wastewater in absorption of CO_2 and its removal from gas phase", Master thesis, Concordia University.

Keller J. and Hartley K. (2003), "Greenhouse gas production in wastewater treatment: process selection is the major factor"; water science technology 47,12: pp 43-48.

Kim J.K., Oh B.R., Chun Y.N., and Kim S.W. (2006), "Effects of Temperature and Hydraulic Retention Time on Anaerobic Digestion of Food Waste", JOURNAL OF BIOSCIENCE AND BIOENGINEERING 102, 4: pp 328–332.

Kuroda M., Watanabe T. (1995), "CO_2 reduction to methane and acetate using a bio-electro reactor with immobilized methanogens and homoacetogens on electrodes" Energy Convers. Mgmt 36: pp 787-790.

LAY J.J, LI Y.Y., and NOIKE T. (1997), "Influences of pH and moisture content on the methane production in high solids sludge digestion" Water Resource, 31, 6: pp 1518- 1524.

Leilieveld J., Lechtenbohmer S., Assonov S.S., Brenninkmeijer C.A.M., Dienst C., Fischedick M., Hanke T. (2005), "Greenhouse gases: low methane leakage from gas pipelines" Nature, 434: pp 841-842.

Leong S.K., Nur F.A.K. (2011), "Effect of Organic Loading Rates on Pulp and Paper Wastewater Treatment Using an Anaerobic Upflow Fixed-Film Reactor", 2010 International Conference on Biology, Environment and Chemistry, IPCBEE, 1: pp 122-125.

Liu Y. (2003), " Chemically reduced excess sludge production in the activated sludge process" Chemosphere 50: pp 1–7.

Maeda K., Owada M., Kimura N., Omata K, and Karube I. (1995), "CO_2 fixation from the flue gas on coal-fired thermal power plant by microalgae", Energy Convers. Mgmt, 36: pp 717-720.

Mahmood T., Elliot A. (2006), "Activated Sludge Process Modification for Sludge Yield Reduction Using Pulp and Paper Wastewater." Journal of Environmental Engineering 132: pp 1019-1027.

Manhokwe S., Parawira W., Tekere M. (2009), "An evaluation of a mesophilic reactor for treating wastewater from a Zimbabwean potato-processing plant" African Journal of Environmental Science and Technology, 3.4: pp 091-096.

Martens P. (published Edited version in 2013), "Health and Climate Change: Modelling the Impacts of Global Warming and Ozone .Depletion", Earthscan Publications Ltd, New York, p. 2.

Mcgranahan G., Balk D., and Anderson B. (2007), "The rising tide: assessing the risks of climate change and human settlements in low elevation coastal zones" Environment and Urbanization, 19.1: pp.17-37.

Metcalf and Eddy (2003), "Wastewater Engineering Treatment & Reuse 4TH Edition", McGraw Hill.

Neelameggham N. R. (2008), "Carbon Dioxide Reduction Technologies: A Synopsis of the Symposium at TMS 2008", JOM 60, No.2.

Niehaus, F. (1978), "The problem of carbon dioxide", IAEA BULLETIN 21, NO.1.

Nygaard J. (1997), "Energy aspects of mechanical pulp, chemical pulp and recycled fibers", Tappi International Mechanical Pulping Conference, Atlanta, GA, Tappi Press.: pp 17-27.

Peters M.S., Timmerhaus K.D. (1991), "Plant design and economics for chemical engineering", McGraw-Hill book company, 4th ed.: Ch4&5.

Pokhrel D., Viraraghavan T. (2004), “Treatment of pulp and paper mill wastewater—a review” Science of the Total Environment, 333: pp 37– 58.

Press W.H., Teukolsky S.A., Vetterling W.T. and Flannery B.P. (1992), "Numerical recipes in C: the art of scientific computing", second edition, Cambridge University, New York.

Ramseur, J.L., Parker L., and Yacobucci B. D. (2008), "Greenhouse Gases: Management, Reduction and Impact", Novinka publisher, p.2.

Rao A. G., Kanth Reddy T. S., Prakash S. S., Vanajakshi J., Joseph J., Sarma P. N. (2007), “pH regulation of alkaline wastewater with carbon dioxide: a case study of treatment of brewery wastewater in UASB reactor coupled with absorber”, Bioresource Technology 98,11: pp 2131-6.

Rapier R. (2012), “Global Carbon Dioxide Emissions - Facts and Figures”, consumer energy report. http://www.consumerenergyreport.com/2012/07/02/global-carbon-dioxide-emissions-facts-and-figures/

Rasi S., Veijanen A., Rintala J. (2007), “Trace compounds of biogas from different biogas production plants” Energy 32: pp 1375–1380.

Reay D., Hewitt C.N., Smith K. and Grace J. (2007), "Greenhouse Gas Sinks", CABI international publisher.

Reeve D.A. (2000), “The Capture and Storage of Carbon Dioxide Emissions.” Office of Energy Research and Development Natural Resources, Ottawa, Canada.

Riebeek, Holli, NASA earth observatory news & notes, (July 6, 2010).

Rittmann B.E., McCarty P.L. (2001), "Environmental biotechnology:Principles and applications", McGraw-Hill, Toronto, Ontario, Canada.

Riviello J. M., (2014)," CO_2-removal device and method", patent publication number: EP2688662 A1, available at: https://www.google.com/patents/EP2688662A1?cl=en&dq=patent+co2+removal+method&hl=en&sa=X&ved=0ahUKEwjdrtXdq-LJAhXG6RQKHcAeCa8Q6AEIKzAC.

Rochelle G., Cullinane J. (2007), "Polyamine/ alkali salt blends for carbon dioxide removal from gas stream" Tx (US), patent publication number: US 2007/0044 A1. http://images2.freshpatents.com/pdf/US20070044658A1.pdf

Roh Y., McMillan A.D., Lauf R.J.and Phelps T.J. (2000), "Utilization of biomineralization processes for carbon sequestration", Abstract for Annual Meeting American Geophysical Union, December 15-19, San Francisco, CA.

Salomoni C., Caputo A., Bonoli M., Francioso O., Rodriguez-Estrada M.T., Palenzona D. (2011), "Enhanced methane production in a two-phase anaerobic digestion plant, after CO_2 capture and addition to organic wastes" Bioresource Technology 102: pp 6443–6448.

Sato K., Ochi S. (1994), "Control of carbon dioxide gas concentration to increase methane gas production in anaerobic sewage sludge digestion." In: Seventh international symposium on anaerobic digestion, Cape Town: pp 610-618.

Saini R., Majhi M. C., Kapoor R., Kumar R. and Kumar A. (2011), "Carbon dioxide (CO_2) utilizing strain database" African Journal of Biotechnology 10.63: pp 13818-13822.

Science Daily, (visited Nov. 2012) http://www.sciencedaily.com/releases/2012/10/121017162420.htm

Shihwu S. (2008), " Anaerobic Water Treatment Technologies" Ph.D., PE, Department of Civil, Construction & Environmental Engineering, Iowa State University, National Cheng Kung University, available at: http://www.wpeiic.ncku.edu.tw/resources/Aeaerobic%20Water%20Treatment.pdf

Shulk B. F. Editor (2007), "Greenhouse Gases and Their Impact" New York: Nova Science: pp 19-20.

Sørensen A.H. and Ahring B.K. (1993), "Measurements of the specific methanogenic activity of anaerobic digestor biomass" Applied microbiology and biotechnology 40: pp 427-431.

Stewart C. and Hessami M.A. (2005), "A study of methods of carbon dioxide capture and sequestration—the sustainability of a photosynthetic bioreactor approach"; Energy Conversion and Management 46: pp 403–420.

Tabatabaei M., Abdul Rahim R., Abdullah N., Wright A.D.G., Shirai Y., Sakai K., Sulaiman A., Ali Hassan M. (2010), "Importance of the methanogenicarchaea populations in anaerobic wastewater Treatments" Process Biochemistry 45,8: pp1214–1225.

Taguchi K., Kajiwara S., Mustaqim D., and Takahashi N. (1997), "Cyanobacterial bioconversion of carbon dioxide for fuel productions", Energy Convers.Mgmt, 38: pp S523-S528.

Tezel U., Guven E., Erguder T.H. , Demirer G.N. (2001), "Sequential (anaerobic/aerobic) biological treatment of Dalaman SEKA Pulp and Paper Industry effluent", Waste Management 21: pp 717–724.

The Biogas Technology in China, BRTC, China (1989). available at: http://www.fao.org/sd/EGdirect/EGre0022.htm

The Guardian, (visited Apr. 2015), available at: http://www.guardian.co.uk/news/datablog/2011/jan/31/world-carbon-dioxide-emissions-country-data-co2

Thompson G., Swain J., Kay M., Forster C.F (2001), "The treatment of pulp and paper mill effluent: a review" Bioresource Technology 77, 3: pp 275–286.

Topo Geo (2012), "Carbon credit". available at: (http://www.carboncredit2012.com/site/index.php/carbon-credit)

Tsilemou K. and Panagiotakopoulos D. (2006), "Approximate cost functions for solid waste treatment facilities." Waste Management and Research 24:310, published by SAGE on behalf of ISWA)

TWBG (The World Bank Group) (1999), "Pollution prevention and abatement handbook".

TWBG (The world bank group) (2014), "State and trend of carbon pricing", Washington DC.

United Nations Industrial Development Organization (UNIDO) and Ministry of International Trade and Industry(MITI) (1993), "handy manual on pulp and paper industry", Output of a Seminar on Energy Conservation in Paper and Pulp Industry Sponsored by Japan.

US EPA, (visited Apr. 2015), available at: http://www.epa.gov/climatechange/ghgemissions/gases/co2.html

US EPA (2012), "2010 Greenhouse Gas Emissions Data from Large Facilities", available at http://yosemite.epa.gov/opa/admpress.nsf/0/8890DDDC08B1B82785257982005CCACD.

US EPA research triangle park, sector policies and programs division office of air quality planning and standards (2010), "Available and emerging technologies for reducing GHG emissions from the pulp and paper manufacturing industry".

U.S. Department of Commerce/International Trade Administration, U.S. Industry & Trade Outlook (2000). U.S. Department of Commerce, McGraw-Hill. 2000.

U.S. Department of Energy (2000), “Forest Products Project Fact Sheet: Closed-Cycle Bleach Kraft Pulp Production.” Office of Industrial Technologies.

Vanloon GW, Duffy SJ. (2011), "Environmental chemistry a global perspective." 3d ed., Oxford University Press.: pp 256-265.

Ward A.J., Hobbs P.J., Holliman P.J., Jones D.L. (2008), “Optimisation of the anaerobic digestion of agricultural resources” Bioresource Technology 99,17: pp 7928–7940.

Wei Y., Van Houten R.T., Borger A.R., Eikelboom D.H. and Fan Y. (2003), " Minimization of excess sludge production for biological wastewater treatment" Water Research 37: pp 4453–4467.

Welander T., Andersson P.E. (1985), "Anaerobic treatment of wastewater from the production of chemi-thermomechanical pulp", Water Sci. Technol., 17: pp 103-111.

Wiegand, P. S. et al. (2011), "Water Profiles of the Forest Products Industry and Their Utility in Sustainability Assessment." TAPPI Journal: pp 19-27.

Wising U. 2003, "Process integration in model Kraft pulp mills: Technical, economical and implications", Chemical engineering and environmental science, Chalmers University of Technology Goteborg.

World Energy Council (2013), "World Energy Resources", (http://www.worldenergy.org/wp-content/uploads/2013/09/Complete_WER_2013_Survey.pdf)

Xuefei Z., Nanqi R. (2007), “Acid resistance of methanogenic bacteria in a two-stage anaerobic process treating high concentration methanol wastewater”, Front. Environ. Sci. Engin. 1,1: pp 53-56.

Yerushalmi L., Ashrafi O. and Haghighat F. (2013), "Reductions in greenhouse gas (GHG) generation and energy consumption in wastewater treatment plants"; Water Science & Technology 67,5: pp 1159-1164.

Web 1:(http://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html)

Web 2: (http://www.globalspec.com/learnmore/manufacturing_process_equipment/air_quality/scrubbers)

Web 3: FRTR remediation technologies screening matrix and references guide, Version 4.0 (http://www.frtr.gov/matrix2/section4/4-60.html)

web 4: http://www.ne-wea.org/LabManual/total_suspended_solids.htm (visited Nov. 2012)

Web 5: from google map (https://www.google.ca/maps/place/Tembec+Matane+Inc./@48.83118,-67.55297,3a,75y,90t/data=!3m5!1e2!3m3!1s-zzggegXoeoM%2FTdhdMU-VnLI%2FAAAAAAAAAV4%2F-r7glMbokZk!2e4!3e15!4m2!3m1!1s0x4c96c0f808e323bb:0x1d0ef0dbab271292?hl=en)

Web 6: (http://www.chemeng.queensu.ca/courses/CHEE332/files/CEPCI_2014.pdf)

Web 7: http://www.metric-conversions.org/volume/us-oil-barrels-to-liters.htm

Web 8: (http://www.engineeringtoolbox.com/heating-values-fuel-gases-d_823.html)

Web 9: (http://www.engineeringtoolbox.com/fuel-oil-combustion-values-d_509.html)

Appendix A: Reference curve for methane content of the biogas

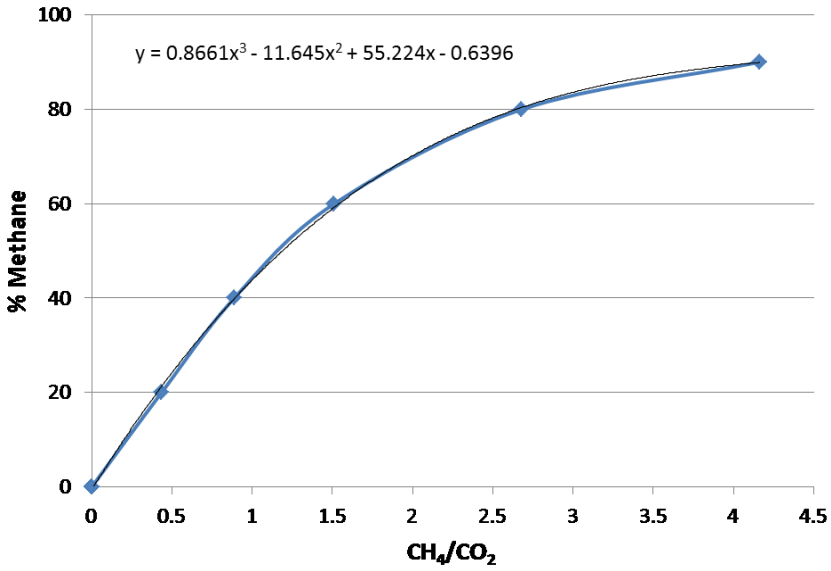


Fig. A.1: Reference curve for methane content of the biogas.

Appendix B: Cost estimation and GHG analysis

All calculations are done based on the data from Tembec Matane treatment plant.

B.1 Information about the Tembec Matane WWTP

Tembec is a large paper company located in Canada (Matane, QC), United States and France with approximately 6000 employees. Tembec has three operating divisions including: forest products, pulp and paper and paper board, and chemicals (produces resins, ethanol, and lignin). Tembec Matane (Fig. 7) is a producer of high yield pulp. Matane is a town with 14500 population and 195km^2 located on the Gaspé Peninsulain, Quebec, Canada, on the south shore of the Saint Lawrence River at the mouth of the Matane River.

Tembec Matane WWTP treats approximately 14000 m^3 WW/d which equals to almost 5×10^6 m^3 WW/y. The produced biomass from anaerobic treatment is equal to 230 m^3/month and is sold at 100$/m^3, bringing financial profit to the plant. However, aerobic reactor produces a large amount of biomass (12 dry tons/day) which is sent to the landfill. There is no solid digestion system in the plant and all produced solids, after dewatering are sent to the landfill. The landfill system is open to air and is not managed for collection of produced biogas from landfill.

The anaerobic treatment is responsible for 65% COD removal and the COD removal reaches 85-90% after aerobic treatment. The plant is very efficient in BOD removal and more than 99% BOD removal after aerobic treatment is reported.

The influent wastewater of anaerobic bioreactor has a temperature around 35°C, which is a favorable temperature for methanogenic bacteria and anaerobic activity. As the wastewater leaves the anaerobic reactor and enters the aerobic reactor, it loses heat. Consequently, the temperature inside the aerobic activated sludge reactor is around 20°C which provides a good environment for aerobic bacteria inside the reactor. Aerobic processes, especially the activated sludge process do not operate properly above 30°C (Ashrafi, 2012). Therefore, the Tembec treatment plant has a proper design that minimizes its energy requirement for heating the wastewater inside the bioreactor.

CTMP samples have small particle sizes that prevent clogging in scrubber nozzles. The mean size of CTMP wastewater measured by a particle size analyzer was 0.287 µm.

The Tembec Matane wastewater treatment plant operates with the capacity of 5138470 m^3/y wastewater and produces 250000 ton dry pulp per year. Therefore, the amount of wastewater produced per ton of pulp is equal to 20.6 m^3 WW/ton of dry pulp as calculated in Appendix B. This value can be compared with other reported values in the literature such as 20-100 m^3 WW production per ton of dry pulp (TWBG 1999). This shows the efficiency of Tembec Matane plant in producing the minimum possible wastewater.

B.1.1 WW production/ton of produced pulp

(5138470m^3/y)/(250000 ton dry pulp/year)= 20.6 m^3 WW/ton of dry pulp

B.2 Conventional hybrid treatment and aerobic treatment processes

B.2.1 Methane production from anaerobic treatment in a conventional hybrid treatment process

By considering the flow to the anaerobic reactor which is 13585 m^3/d as well as the COD of wastewater which is 10.2 g/l, the amount of COD that enters the anaerobic reactor would be 138.6 t COD/d.

$$(10200 \times 10^{-9} \frac{ton\ COD}{L}) \times \frac{13585 m^3}{d} \times \frac{1000 L}{m^3} = 138.6\ \frac{ton\ COD}{d} eneter\ the\ anaerobic\ reactor$$

With regard to the plant information, 65% COD is removed in the anaerobic reactor and 0.4 m^3 CH_4/kg COD_{rem} is produced. Therefore, the methane generation from this reactor is equal to 13150008 m^3 CH_4/y (Rounded to 13 M m^3 CH_4/y).

$$\left(138.567\ \frac{ton\ COD}{d}\right) \times \left(\frac{1000 kg}{1 ton}\right) \times (0.65\ COD\ removal\ from\ anaerobic\ treatment) \times \left(0.4\ \frac{m^3\ CH_4\ produced}{kg\ COD_{rem}}\right)$$

$$= 36027.4 \frac{m^3\ CH_4\ produced}{d} = 13150008 \frac{m^3\ CH_4\ produced\ from\ anaerobic\ treatment}{y}$$

B.2.2 Recovered methane from anaerobic treatment in a conventional hybrid treatment process

By considering 95% efficiency in the recovery of produced methane in the anaerobic treatment, approximately 12.5 million m^3 CH_4 is recovered per year.

$$36027.4\frac{m^3\ CH_4\ produced}{d} \times\ 0.95\ recovery\ of\ the\ gas = 34226\frac{m^3\ CH_4\ recovered\ from\ anaerobic\ digestion}{d}$$

$$= 12492508\frac{m^3\ CH_4\ recovered}{y}$$

B.2.3 Methane leaked from anaerobic treatment in a conventional hybrid treatment process

The magnitude of methane leak through the methane recovery process in anaerobic treatment, which is 5% of the generated methane, is equal to 657500 m^3 CH_4 per year. The leaked CH_4 enters the atmosphere and is considered as a GHG.

$$36027.4\frac{m^3\ CH_4\ produced}{d} \times\ 0.05\ leak\ of\ biogas = 1801.4\frac{m^3\ CH_4\ leaked}{d} = 657500.4\frac{m^3\ CH_4\ leaked\ to\ the\ atmosphere}{y}$$

B.2.4 CO_2e of methane leaked from anaerobic treatment in a conventional hybrid treatment process

Considering that the GWP for CH_4 is 21 and its density is 0.66 kg/m^3, the equivalent carbon dioxide of the leaked methane is calculated to be 9112956 kg CO_2e/y. This value defines the GHG generated during anaerobic treatment.

$$657500.4\frac{m^3\ CH_4\ leaked}{y} \times\left(\frac{0.66\text{kg}}{1m^3\ CH_4}\right)\times\left(\frac{21\ kg\ CO_2e}{1\ kg\ CH_4}\right) = 9112956\frac{kg\ CO_2e}{y}$$

B.2.5 CO_2 emission from anaerobic treatment in a conventional hybrid treatment process

In this study, 70 to 75% of the gas emission from anaerobic bioreactor belongs to methane, which corresponds to 13150008 m^3 CH_4/y. Accordingly, the remaining 25% CO_2 emission is equal to 4383336 m^3 CO_2/y (8679005.3 $kgCO_2/y$).

$$\left(13150008\ \frac{m^3\ CH_4}{\text{y}}\right)\times\left(\frac{0.25m^3\ CO_2}{0.75m^3\ CH_4}\right)=4383336\ m^3\ CO_2/\text{y}$$

$$\left(4383336\ \frac{m^3\ CO_2}{\text{y}}\right)\times\left(\frac{1.98\text{kg}}{m^3}\right)=8679005.3\ \text{kg}\ CO_2/\text{y}$$

B.2.6 Energy production from the retrieved methane from anaerobic treatment in a conventional hybrid treatment process

The heating value and the density of methane are reported to be 50 TJ/kiloton (Web 8) and 0.66kg/m^3, respectively. Therefore the potential energy generation from the combustion of recovered methane is approximately 412 TJ/y (=1.15×10^8 kWh/y)

$$12492508\frac{m^3\ CH_4\ recovered}{year}\times\left(\frac{0.66kg}{m^3}\right)\times\left(\frac{1kton}{10^6kg}\right)\times\left(\frac{50TJ}{kiloton}\right)=412.25\frac{TJ}{y}=\frac{1.15\times10^8kWh}{y}produced$$

B.2.7 Energy requirement of anaerobic treatment in a conventional hybrid treatment process

By referring to the information provided by the treatment plant, 13585m^3 WW/d enters the anaerobic bioreactor with the retention time of 7h. Therefore, the volume of anaerobic reactor can be calculated as below:

$$\text{Reactor working volume (V)}=\text{Q.t}=\left(\frac{13585\text{m}^3}{\text{d}}\right)\times\left(\frac{1\text{d}}{24\text{hr}}\right)\times(7\text{hr})=3962.3\text{m}^3$$

$$\text{Overal power required for anaerobic treatment}=\left(\frac{0.01\text{kW}}{\text{m}^3\text{ reactor volume}}\right)\times(3962.3\text{m}^3)\times(8760\text{hr/y})=347097\ \text{kWh/y}$$

B.2.8 Energy production/kg COD removed from anaerobic treatment in a conventional hybrid treatment process

A standard method for reporting energy production in a plant is to define it per COD removed. This method of reporting enables the comparison of energy production in different plants based on their efficiency in methane generation by anaerobic treatment. Considering 0.4 m^3 methane produced per kg COD removed, and 95% biogas recovery, the energy generation from the

combustion of recovered methane from anaerobic treatment is calculated to be 12.54×10^{-6} TJ/kg COD_{rem} (3.483 kWh/kg COD_{rem}).

This value can be compared to similar values from other plants. Snug (2008) reported 1.16 kWh/kg COD_{rem} in the anaerobic treatment of wastewater. Tembec Matane WWTP has three times higher methane generation from anaerobic treatment which shows its high efficiency in this process.

$$\left(0.4\ \frac{m^3\ CH_4\ produced}{kg\ COD_{rem}}\right)\times(0.95\ biogas\ recovered)\times\left(\frac{0.66kg\ CH_4}{m^3}\right)\times\left(\frac{1kton}{10^6kg}\right)\times\left(\frac{50TJ}{kton}\right)=12.54\times10^{-6}\frac{TJ}{kg\ COD_{rem}}$$
$$=3.483\ kWh/kg\ COD_{rem}$$

B.2.9 Saving in light oil fuel consumption from anaerobic treatment in a conventional hybrid treatment process

With reference to the heating value of light oil which is 14500 btu/gal ($40x10^{-6}$ TJ/kg) (Web 9) as well as the density of oil which is approximately 875.7 kg/m^3, the amount of fossil fuel (light oil) saved by the combustion of recovered methane from anaerobic treatment, replacing light oil, is calculated to be 11.8×10^6 l oil/y :

$$\left(412.25\frac{TJ}{y}\right)\times\left(\frac{1\ kg\ light\ oil}{40\times10^{-6}TJ}\right)\times\left(\frac{1000l}{875.7\ kg}\right)=11.8\times10^6\frac{l\ oil}{y}$$

B.2.10 GHG emission from power production from anaerobic treatment in a conventional hybrid treatment process

By assuming that the required energy for the anaerobic treatment is provided by electricity, and knowing that 0.96 kg CO_2 is generated per each kWh electricity generation, then the total CO_2 generation from energy generation (347097 kWh/y) for anaerobic treatment is equal to 333213 kg CO_2/y.

$$CO_2\ production\ from\ power\ generation\ in\ anaerobic\ treatment=\left(0.96\frac{CO_2}{kWh}\right)\left(\frac{347097kWh}{y}\right)=333213\ kg\ CO_2/y$$

If the entire recovered methane is burnt, it produces 109923549 kg CO_2/y which is not considered as GHG.

$$CO_2\ production\ from\ combustion\ of\ recovered\ methane=\left(0.96kg\frac{CO_2}{kWh}\right)\left(\frac{114503697kWh}{y}\right)=109923549\ kg\ CO_2/y$$

B.2.11 CO_2e of methane recovered from anaerobic treatment in a conventional hybrid treatment process

Methane generated in the anaerobic treatment process serves as a GHG if it enters the atmosphere. However, the recycling of methane offsets this emission. The carbon dioxide equivalent of the recovered methane is calculated to be 173146159 kg CO_2e/y.

$$12492508\frac{m^3\ CH_4\ recycled}{year}\times\left(\frac{0.66\text{kg}}{1m^3\ CH_4}\right)\times\left(\frac{21\ kg\ CO_2}{1\ kg\ CH_4}\right)=173146159\frac{kg\ CO_2e}{y}$$

B.2.12 CO_2e offset from the combustion of recovered methane instead of fossil fuel in a conventional hybrid treatment process

The combustion of recovered methane from anaerobic treatment and its use as a source of energy reduces or eliminates the demand for burning of fossil fuel, as well as its associated CO_2 emission which is a GHG. On the other hand, the CO_2 generated during the combustion of recovered methane is not considered as a GHG. In fact, the combustion of recycled methane instead of light oil causes GHG reduction equal to 23045 tons CO_2e/y. This CO_2e offset equals to the amount of CO_2 that could be produced by burning gasoline (as light oil) to generate the same amount of energy as the combustion of recovered methane.

$$(412.3\ TJ\ from\ recycled\ methane\ combustion/y)\times(68.6\ t\ CO_2/TJ)=23045\ tons\ CO_2e/y$$

For this calculation, the IPCC emission factor for gasoline as a light oil (69.3 tCO_2/TJ) is used which is equal to 68.6 metric tons CO_2/TJ (after correcting for 1% un-oxidized carbon 69.3×0.99=68.6) (NCASI, 2005).

B.2.13 CO_2 emission from BOD removal in aerobic reactor

The equations for the aerobic carbonaceous BOD and biomass decay are as follow:

$$0.02C_{10}H_{19}O_3N+0.01NH_4^+ +0.01HCO_3^- +0.1O_2\rightarrow 0.03C_5H_7O_2N+0.11H_2O+0.06CO_2$$

$$0.05C_5H_7O_2N+0.25O_2\rightarrow 0.2CO_2+0.05NH_4^+ +0.05HCO_3^- +0.05H_2O$$

Based on the first equation, when removing 0.02 mol BOD from wastewater, 0.06 mol CO_2 and 0.03 mol biomass is produced from the aerobic bioreactor. It implies that when removing 1g BOD (MM=201g/mol) from wastewater, 0.66g CO_2 (MM=44g/mol) and 0.84g biomass (MM=113g/mol) are produced from the aerobic bioreactor. By assuming that the growth yield coefficient of aerobic biomass is 0.5 which means that 0.5g biomass generated per gram of removed BOD (Liu, 2003; Wei et al., 2003), and having in mind that 1g BOD produces 0.84g biomass, 0.34g biomass decay/g BOD removal is expected (0.84-0.50=0.34). Based on second equation, 0.05 mole biomass decay can produce 0.2 mole CO_2 which means 0.34 g biomass decay can produce 0.53g CO_2. In other word, by aerobic digestion, each 1g BOD removed incorporated into 0.84g new biomass or is biologically oxidized to 0.66 g CO_2. A fraction of the biomass (equal to 0.34g biomass) can further produce 0.53g carbon dioxide via endogenous respiration.

Therefore the total carbon dioxide emission from aerobic bioreactor would be the summation of these two portions and is equal to 1.19g CO_2/g BOD removal (0.66+0.53).

- **CO_2 emission from biological oxidation of wastewater in aerobic reactor:**

$$1g\ BOD \times \left(\frac{1\ mole}{201g\ BOD}\right) \times \left(\frac{0.06\ mole\ CO_2}{0.02\ mole\ substrate}\right) \times \left(\frac{44g\ CO_2}{1mole\ CO_2}\right) = 0.66\ \frac{g\ CO_2}{g\ BOD\ removed}$$

- **CO_2 emission from biomass decay in aerobic reactor:**

$$\frac{0.34\ g\ decayed\ biomass}{g\ BOD\ removed} \times \left(\frac{0.2\times44\ g\ CO_2}{0.05\times113g\ decayed\ biomass}\right) = 0.53\ \frac{g\ CO_2}{g\ BOD\ removed}$$

B.2.14 CO_2 emission from aerobic bioreactor in a conventional hybrid treatment systems

For hybrid systems, if we assume 85% BOD removal in the anaerobic reactor and 15% BOD removal in aerobic reactor, therefore 4.4×10^9 gCO_2/y emission from aerobic bioreactor is expected.

$$(67.6 \times 10^6 g\ BOD/d) \times \left(\frac{365d}{y}\right) \times (0.15\ BOD\ removal) \times \left(\frac{1.19\text{g } CO_2}{\text{g BOD removed}}\right) = 4.4 \times 10^6\ \text{kg}CO_2/\text{y}$$

B.2.15 CO_2 emission from aerobic bioreactor if the only treatment system is aerobic treatment

If the only treatment system is aerobic treatment with 95% BOD removal efficiency, the CO_2 emission from the aerobic reactor would be 2.79×10^7 kg CO_2/y.

$$(67.6 \times 10^6\ g\ BOD/d)\left(\frac{365d}{y}\right)(0.95\ BOD\ removal)\left(\frac{1.19\ g\ CO_2}{g\ BOD\ removed}\right) = 2.79 \times 10^7 kg\ CO_2/y$$

B.2.16 CH_4 generation from landfill when hybrid treatment process is applied

In this work, for the estimation of GHG emission, a simplified first order decay approach is used, which is the default recommended method by the IPCC (IPCC 2000a). This method can be used for the estimation of GHG emissions from active and inactive landfills. This simplified method can be applied in cases where the type of waste disposed to the landfill remains unchanged, hence the annual deposit is constant. The first order decay approach is subsequently reduced to two equations as follows (NCASI, 2005):

$$CH_4(m^3/y)\ generated\ from\ all\ waste\ in\ the\ landfill = R\ L_0(e^{-kC} - e^{-kT})$$

$$where:\ R = average\ amount\ of\ waste\ sent\ to\ landfill\ per\ year, \frac{Mg}{y}$$

$$L_0 = ultimate\ methane\ generation\ potential, m^3/Mg\ waste$$

$$k = methane\ generation\ rate\ constant, \frac{l}{y}$$

$$C = time\ since\ landfill\ stopped\ receiving\ waste, y$$

$$T = years\ since\ landfill\ opened, y$$

Recommended default values for k and L_0 for estimating landfill methane emissions are (NCASI, 2005):

k=0.03 y^{-1} and

L_0=100m^3/Mg dry weight of waste.

If the landfill has a gas collection system, the generated methane from the landfill can be recovered. The amount of methane released to the atmosphere will be the total gas generation from the landfill minus the collected gas, as presented below:

$$CH_4(m^3/y)\ released = [(CH_4\ generated - CH_4\ recovered) \times (1 - OX)] + [CH_4\ recovered \times (1 - FRBURN)]$$

$$where: CH_4\ generated = from\ last\ equation$$

$$CH_4\ recovered = amount\ of\ methane\ collected, site\ specific\ determination$$

$$OX = fraction\ oxidized\ in\ the\ surface\ layer\ of\ the\ landfill\ before\ escaping, usually\ assumed\ to\ be\ o.1$$

$$FRBURN = fraction\ of\ collected\ methane\ that\ is\ burned, site\ specific\ determination.$$

In the treatment plant examined in this study, the landfill is not equipped with a gas collection system and all produced gas is released to the atmosphere. Therefore, the previous equation simplifies to the following equation:

$$CH_4 released(m^3/y) = CH_4\ generated \times (1 - OX)$$

By assuming T=50 years since the landfill started operation, and C=0 since the landfill is continuously receiving the waste, 340268.99 m^3 CH_4/y is generated from landfill when hybrid treatment process is applied. Therefore the methane release to the atmosphere would be 306242 m^3 CH_4/y which is equal to 4244514 kg CO_2e/y.

$$CH_4\ generated\ from\ landfill(\mathrm{m^3/y}) = (4380\ \mathrm{Mg\ dry\ waste/y})\left(100\frac{\mathrm{m^3\ methane}}{\mathrm{Mg\ dry\ weight\ of\ waste}}\right)(0.777) = 340268.99\ \mathrm{m^3\,CH_4/y}$$

and,

$$CH_4\ released\ to\ atmosphere\ from\ landfill(\mathrm{m^3/y}) = (340268.99\ \mathrm{m^3\,CH_4/y})(1 - 0.1) = 306242\ \mathrm{m^3\,CH_4/y}$$

Then the CO_2e of this methane released to the atmosphere is equal to 4244514 kg CO_2e/y as calculated below:

$$306242 \frac{m^3\ CH_4}{year} \times \left(\frac{0.66\text{kg}}{1m^3\ CH_4}\right) \times \left(\frac{21\ kg\ CO_2e}{1\ kg\ CH_4}\right) = 4244514 \frac{kg\ CO_2e}{y}$$

B.2.17 Energy saving and CO_2e offset by collection of methane released from the landfill in a hybrid treatment process

If the landfill was equipped with a gas collection system and the generated methane from the landfill was collected, this CH_4 could be used as a source of energy to produce approximately 10TJ energy and save $350902 per year. On the other hand, by considering the emission factor of natural gas for methane which is 55.9 tCO_2/TJ, it is shown that this collection of methane could offset 564.92 ton CO_2e/y and produce 10.106 TJ/y energy, as calculated below:

Energy saving from combustion of recovered methane from covered landfill would be equal to:

$$306242 \frac{m^3\ CH_4}{year} \times \left(\frac{0.66kg}{m^3}\right) \times \left(\frac{1kton}{10^6 kg}\right) \times \left(\frac{50TJ}{kiloton}\right) = 10.1\ TJ/y$$

Then the CO_2 offset from this energy recovery is as calculated bellow:

$$(10.1\ TJ/y) \times (55.9\ t\ CO_2/TJ) = 564.9\ tonne\ CO_2/y$$

And the saving by recovery of methane release from landfill would be:

$$10.1 \frac{TJ}{y} \left(\frac{277777.8\ kWh}{1TJ}\right) \left(\frac{0.125\$}{kWhr}\right) = 350902\$/y$$

B.2.18 Solid biomass generation from aerobic treatment as the only treatment method

$$\left(67.6\ ton \frac{BOD}{d}\right) \times (0.95\ BOD\ removal\ efficiency) \times \left(\frac{0.5\ ton\ dry\ AS}{1\ ton\ BOD\ removed}\right) = 32.1\ \frac{ton\ dry\ activated\ sludge}{d}$$
$$= 11720\ ton\ dry\ AS/y$$

The obtained value for sludge production by aerobic treatment could be compared to the similar value for sludge production when hybrid treatment (anaerobic/aerobic) is applied. By applying hybrid treatment, sludge produced from aerobic treatment would be 4380 dry ton/year (equal to 17520 m^3/y) and the sludge from anaerobic treatment reactor would be 2760 m^3/y which is negligible compared to the amount produced in the aerobic bioreactor. Consequently, the

application of hybrid system instead of aerobic treatment, leads to the elimination of 7340 ton dry AS/y (63% reduction in the production of AS)

B.2.19 Methane generation from the studied landfill, if the only treatment method is aerobic treatment

$$CH_4\ generated\ from\ landfill(\mathrm{m^3/y}) = \left(11720.15\ ton\ dry\frac{AS}{y}\right)\left(100\frac{\mathrm{m^3\,methane}}{\text{ton dry weight of waste}}\right)(0.777) = 910655.7\ \mathrm{m^3\,CH_4/y}$$

And,

$$CH_4\ released\ to\ atmosphere\ from\ landfill(\mathrm{m^3/y}) = (910655.7\ \mathrm{m^3\,CH_4/y})(1-0.1) = 819590\ \mathrm{m^3\,CH_4/y}$$

Then the CO_2e of this methane released to the atmosphere is equal to 11359517 kg CO_2e/y as calculated below:

$$819590\frac{m^3\ CH_4}{year}\times\left(\frac{0.66\mathrm{kg}}{1m^3\ CH_4}\right)\times\left(\frac{21\ kg\ CO_2e}{1\ kg\ CH_4}\right) = 11359517.4\frac{kg\ CO_2e}{y}$$

B.2.20 Energy saving and CO_2e offset by collection of methane released from the landfill in a aerobic treatment process as the only treatment method

Energy saving from combustion of recovered methane from covered landfill would be equal to:

$$819590\frac{m^3\ CH_4}{year}\times\left(\frac{0.66kg}{m^3}\right)\times\left(\frac{1kton}{10^6kg}\right)\times\left(\frac{50TJ}{kiloton}\right) = 27\ TJ/y$$

Then the CO_2 offset from this energy recovery is as calculated bellow:

$$(27\ \ TJ/y)\times(55.9\ t\ CO_2/TJ) = 1511.9\ tonne\ CO_2/y$$

And the saving by recovery of methane release from landfill would be:

$$27\frac{TJ}{y}\left(\frac{277777.77777778\ kWh}{1TJ}\right)\left(\frac{0.125\$}{kWh}\right) = 939097.2\$/y$$

B.2.21 Power required for aerobic treatment as the only treatment method

$$\left(1.5\frac{kWh}{kg\ COD\ removed}\right)\times\left(138.6\times10^3\frac{kg\ COD}{d}\right)(0.80)\times\left(\frac{365d}{y}\right) = 60692346kWh/y$$

B.2.22 Power required for aerobic treatment in the hybrid treatment process

$$\left(1.5\frac{kWh}{kg\ COD\ removed}\right)\times\left(138.6\times10^{3}kg\frac{COD}{d}\right)(0.20)\times\left(\frac{365d}{y}\right)=15173086.5kWh/y$$

B.2.23 Cost of aerobic treatment sludge disposal to the landfill in a hybrid treatment process

$$\left(4380\times10^{3}\frac{kg\ dry\ sludge}{year}\right)\times\left(\frac{m^{3}}{250\ kg\ dry\ sludge}\right)\left(\frac{17\$}{m^{3}}\right)=297840\ \$/year$$

B.2.24 Cost of sludge disposal to the landfill in aerobic treatment as the only treatment process

$$\left(11720\times10^{3}\frac{kg\ dry\ sludge}{year}\right)\times\left(\frac{m^{3}}{250\ kg\ dry\ sludge}\right)\left(\frac{17\$}{m^{3}}\right)=796960\ \$/year$$

B.3 Developed process

B.3.1 CO_2 emission from Tembec Matane CTMP plant

The required energy for Tembec Matane CTMP plant originates from two sources:

- Electricity : 2039 kwh per ton of pulp (7.3 GJ/ton of pulp)
- Fossil fuel: 0.5 GJ/t of pulp (139kWh/ton of pulp)

The plant produces 250000 ton dry pulp per year, therefore by considering 2039 kWh/ t pulp, the total electricity required in one year for the pulp producing plant will be 509750000kWh/y.
Based on the assumption that CO_2 emission from electricity generation is equal to 0.96 kg CO_2/kWh, the total CO_2 emission from electricity generation for CTMP plant in one year is equal to 489,360 tCO_2. On the other hand, fossil fuel combustion in the Tembec Matane CTMP plant produces 0.5 GJ/t of pulp. Knowing that the plant produces 250000 ton dry pulp per year, this results in 125000 GJ energy generation from fossil fuel combustion per year for the pulping plant.

By assuming the use of gasoline as a fossil fuel for energy generation, and by considering the IPCC emission factor for gasoline as light oil (68.6 metric tons CO_2/TJ), the CO_2 emission from fossil fuel combustion in the pulping plant is equal to 8575 t CO_2/y. Therefore, the total CO_2 emission from energy generation (electricity generation and fossil fuel combustion) for the CTMP pulping plant would be 489,369 tCO_2/y. Considering the density of CO_2 to be 1.98kg/m^3, the CO_2 emission from energy generation processes will be 247,155,846 m^3 CO_2.

B.3.2 Total gas that passes through the scrubber in order to dissolve CO_2 emission from energy generation in wastewater

By assuming that CO_2 emission from power generation (which equals to 247 million m^3 CO_2/y) is 60% of total the flue emission gases, the total gas that passes through the scrubber in order to dissolve CO_2 emission from the CTMP plant in wastewater would be 27677 ft^3gas/min (cfm):

$$(247155846\ m^3\ CO_2/y) \times \left(\frac{100\ m^3\ gas}{60\ m^3\ CO_2}\right) = 411926410\ m^3\ gas/y = 14547043879\ ft^3\ gas/y = 27677\ ft^3\ gas/\ min\ (cfm)$$

B.3.3 Required wastewater to pass through the scrubber in one year

Based on the results presented in Table 2.6, a spray scrubber requires 1 to 20 gal wastewater per each 1000 cubic feet of gas that passes through it. Therefore, the required wastewater to pass through the scrubber in one year and be in contact with the gas emitted from pulping plant will be 14547044 to 290940877 gal WW/y:

$$(14547043879\ ft^3\ gas/y) \times \left(\frac{1-20\ gal\ WW}{1000\ ft^3\ gas}\right) = 14547044\ to\ 290940877\ gal\ WW/y = 55066.6\ to\ 1101331\ m^3\ WW/y$$

It should be noted that the total wastewater entering the anaerobic reactor is 5150000 m^3/y compared to the amount of wastewater that should pass the scrubber to dissolve the CO_2 emission from the plant. Therefore, it is assumed that injection of CO_2 doesn't make a significant change in the pH of anaerobic reactor and doesn't decrease the methanogenic activity in the anaerobic reactor.

B.3.4 CO_2 that could be dissolved in wastewater entering the scrubber

Kazemi (2013) studied CO_2 dissolution in CTMP wastewater with the initial pH of 6.5 at 35°C using a gas with 60% CO_2 content and showed that by applying a scrubber without an alkaline solution the concentration of aqueous CO_2 would be 10.3kg CO_2/m^3 WW. On the other hand, the aqueous concentration of CO_2 at 35°C is 1.4g/l wastewater without using a scrubber (≈9g less). Consequently the wastewater that enters the scrubber could dissolve 495599 to 9911979 kg CO_2/y (carbon offset):

$$(55066.6\ to\ 1101331\ \ m^3\ WW/y) \times \left(\frac{9kg\ CO_2}{m^3\ WW}\right) = 495599\ to\ 9911979\ kg\ CO_2\ dissolved/y$$

and the carbon credit for this carbon offset will be:

$$(496\ to\ 9912\ tCO_2/y) \times \left(\frac{6.5\$}{tCO_2e}\right) = 3{,}224 \text{ to } 64{,}428\ \$/y$$

B.3.5 Required power for the scrubber in one year

According to Table 2.6, the power consumption by the scrubber is 1hp/1000cfm. Therefore the required power for the scrubber in one year is equal to 20638.75 watt:

$$\left(\frac{14547043879\ ft^3\ gas}{y}\right) \times \left(\frac{1hp}{1000\ ft^3/min}\right) \times \left(\frac{1y}{525600min}\right) = 27.68\ hp = 20638.75\ watt$$

Then required energy for scrubber in one year is equal to 180795.5 kWh/y (650863725.5 kJ/y).

By assuming the cost of power generation to be 0.125$/kWh, the cost of providing the required energy for scrubber operation in one year will be 22599$/y.

If the energy demand in the scrubber is supplied by electricity, the resulted CO_2 emission will be:

$$(180795.5\ kWh) \times \left(\frac{0.96\ kg\ CO_2}{kWh}\right) = 173563.68\ kg\ CO_2/y$$

If electricity is provided by combustion of recovered methane from anaerobic reactor, then the CO_2 emission from power generation for the scrubber is not considered as a GHG.

B.3.6 Excess methane generation as a result of CO_2 saturation of wastewater in anaerobic reactor in the developed process

By applying a scrubber, from 496 to 9,912 tCO_2/y was dissolved in the wastewater and was consequently converted to methane by anaerobic biological treatment. According to the results of continuous experiment, up to 97% of the excess dissolved CO_2 as a result of applying a scrubber could be removed. To simplify the calculations we assumed that all excess dissolved CO_2 is removed. Knowing that each mole of CO_2 can be converted to 1 mole of methane, the excess methane generation as a result of CO_2 saturation of wastewater in anaerobic reactor is expected to be equal to 273057 to 5461145 m^3 CH_4/y:

$$\left(495599\ to\ 9911979\ \frac{kg\ CO_2\ dissolved\ by\ scrubber}{y}\right)\times\left(\frac{1mol\ CO_2}{0.044kg\ CO_2}\right)\times\left(\frac{1\ mol\ CH_4}{1\ mol\ CO_2}\right)\times\left(\frac{16\ g\ CH_4}{1\ mol\ CH_4}\right)\times\left(\frac{1m^3 CH_4}{0.66\times10^3 g}\right)$$

$$=273057\ to\ 5461145\ m^3\ CH_4/y$$

This value is compared to the CH_4 generation from anaerobic reactor of hybrid treatment system without applying scrubber, which is equal to 13150008 m^3 CH_4/y. This comparison demonstrates that as a result of CO_2 saturation of wastewater in the developed method, CH_4 generation in anaerobic reactor will increase by 2 to 41%.

By assuming 5% CH_4 leak from the anaerobic reactor, the increase in methane generation results in 13652.85 to 273057.25 m^3 additional CH_4 leak (189228.501 to 3784573.485 kg CO_2e/y) from anaerobic reactor in the developed process compared to the hybrid treatment system.

The CH_4 leak from anaerobic reactor in the hybrid treatment system without scrubber was calculated to be 657500.4 m^3 CH_4/y (9112956 kg CO_2e/y). Therefore the total CH_4 leak from anaerobic reactor in the developed process would be 671153 to 930558 m^3 CH_4/y (9302184.501 to 12897529.485 kg CO_2e/y). This emission is considered as GHG emission.

By the same reasoning and assuming 95% CH_4 recovery from the anaerobic reactor, the increase in methane generation by the saturation of wastewater with CO_2 results in 259404.15 to 5188087.75 m^3 additional CH_4 recovery (3595341.5 to 71906896 kg CO_2e/y) in the developed process compared to the hybrid treatment system.

The total recovered CH_4 from the anaerobic reactor in the developed treatment system will be 12751912 to 17680596 m^3 recovered CH_4/y (=176741501 to 245053055.5 kg CO_2e/y). The retrieved methane is not considered as a GHG emission because it does not enter the atmosphere.

B.3.7 Energy equivalent of the excess recycled methane combustion in the developed hybrid treatment system

$$259404\ to\ 5188088\frac{m^3\ CH_4\ recycled}{year}\times\left(\frac{0.66kg}{m^3}\right)\times\left(\frac{1kton}{10^6kg}\right)\times\left(\frac{50TJ}{kton}\right)=8.56033695\ to\ 171.20689575\ TJ/y$$

$$=2377871\ to\ 47557471\frac{kWh}{y}produced$$

The energy equivalent of the total combusted methane recovered from anaerobic treatment in the developed process will be:

$$\left[\left(8.56\ to\ 171.2\frac{TJ}{y}\right)+412.3\ TJ/y\right]=420.9to\ 583.5\ TJ/y$$

B.3.8 CO_2 emission from combustion of the recovered CH_4

The CO_2 emission from combustion of the excess recovered CH_4 from anaerobic reactor by applying the scrubber in the hybrid treatment system will be equal to:

$$\left(0.96\frac{kg\ CO_2}{kWh}\right)\left(\frac{2377871\ to\ 47557471\ kWh}{y}\right)=2{,}282{,}756\ to\ 45{,}655{,}172\ kg\ CO_2/y$$

The CO_2 emission from combustion of the total recovered CH_4 from anaerobic reactor in the hybrid treatment system will be equal to:

$$CO_2\ production\ from\ combustion\ of\ recycled\ methane=\left(0.96kg\frac{CO_2}{kWh}\right)\left(\frac{2377871\ to\ 47557471\ kWh}{y}+\frac{1.15\times10^8kWh}{y}\right)$$

$$=112682756\ to\ 156055172\ kg\ CO_2/y$$

This CO_2 emission is not GHG emission.

B.3.9 Calculation of saving in light oil fuel consumption by combustion of excess recovered methane in the developed process

With reference to the heating value of light oil which is 14500 btu/gal (=40*10^{-6} TJ/kg) (Web 9) as well as the density of the oil which is around 875.7 kg/m^3, the amount of fossil fuel (light oil in this case) saved by the combustion of excess recovered methane from anaerobic treatment as a

result of applying a scrubber and its use as a source of fuel instead of light oil can be calculated as:

$$\left(8.56033695 \text{ to } 171.20689575 \frac{\text{TJ}}{\text{y}}\right) \times \left(\frac{1 \text{ kg light oil}}{40 \times 10^{-6} \text{TJ}}\right) \times \left(\frac{1000 \text{ l}}{875.7 \text{ kg}}\right) = 244{,}386 \text{ to } 4{,}887{,}715 \text{ l oil/y}$$

The total saving in light oil fuel consumption by combustion of total recovered methane from anaerobic reactor for the developed treatment system is equal to:

$$\left(420.9 to\ 583.5\ \frac{TJ}{y}\right) \times \left(\frac{1\ kg\ light\ oil}{40 \times 10^{-6} TJ}\right) \times \left(\frac{1000 l}{875.7\ kg}\right) = 12 - 16.7 \times 10^{6}\ \frac{l\ oil}{y}$$

By assuming the cost of light oil to be 0.26$/l, the recovered methane in the developed process saves 3.1 to 4.3 M$/y.

B.3.10 Carbon offset in the developed process

There are two sources for carbon offset in developed process:

a) CO_2e offset from bioconversion of dissolved CO_2 to methane:

The CO_2 generated from power generation in the CTMP plant is considered as GHG. By dissolving this carbon dioxide in wastewater and its bioconversion into methane in anaerobic reactor, the atmospheric concentration of CO_2 decreases (carbon offset). By applying a scrubber, from 496 to 9912 tCO_2 was dissolved in the wastewater and was consequently converted to methane by anaerobic biological treatment. On the other hand, the power required for scrubber is provided by combustion of recovered methane from anaerobic reactor and is not a GHG. Therefore, the net CO_2 offset by applying a scrubber would be 496 to 9912 tCO_2/y.

b) CO_2e offset from the combustion of recovered methane, replacing fossil fuels:

The combustion of fossil fuels releases CO_2 as GHG to the atmosphere. In contrast, the CO_2 emission from the combustion of biogas is not considered as GHG emission and is carbon neutral. By capturing the biogas generated in anaerobic reactor and burning it instead of fossil fuel as a source of energy, the carbon offset would be equal to:

$$\left(421\ to\ 583.5 \frac{TJ}{y} from\ recycled\ methane\ combustion\right) \times \left(68.6\ t \frac{CO_2}{TJ}\right) = 28871\ to\ 40029\ tons\ CO_2e/y$$

The total carbon offset from developed system therefore would be the summation of CO_2 offsets from two mentioned sources with the value of 29,365 to 49,940 tCO_2e/y.

Appendix C: Output results of GoldSET software

The output results of GoldSET software is presented below:

C.1 PROJECT DESCRIPTION

C.1.1 Project Objectives and Constraints

- **Project Objective**

  Development of a sustainable process for CO_2 reduction by applying anaerobic treatment./ Performing the cost study and GHG analysis for the developed process in a hybrid treatment system and compare the values with aerobic treatment as the only treatment system, as well as conventional hybrid treatment process.

- **Input Water Characteristics**

  CTMP pulp and paper wastewater. In the CTMP plant, they pre-treat wood chips or other plant material like straw with sodium carbonate, sodium hydroxide, sodium sulfite, and other chemical prior to refining with equipment similar to a mechanical mill. We use output of primary clarifier.

- **Discharge Point(s)**

  The south shore of Saint Lawrence river.

- **Timing and Duration**

  30 Years

C.1.2 General Site Description

- **Zoning and Surroundings**

Tembec Matane is located on the south shore of the saint Lawrence river at the mouth of Matane river. Matane is a town on the Gaspe Quebec, Canada with 14500 population and 195 km^2.

C.2 INDICATOR SELECTION AND WEIGHTING

C.2.1 Indicator Selection

The indicators are presented per dimension in the following tables.

Table C.1 : Dimension Environmental - List of Selected Indicators.

Code	Theme	Indicator	Description	Scoring Scheme
ENV-1	Solid outputs (outputs from the system)	Quality of Solid Waste	Assesses the quality of the discharged solid waste. Assesses the quality of all solid outputs including wastes, byproducts and other solid output materials. Include adherence to local regulations / guidelines here. Also include Toxicity, BOD, COD, pH, N, P, heavy metals). Account for any post-treatment steps required here in order to meet regulations.	0 = Solid waste generated is considered as hazardous residual material. 60 = Solid waste generated is considered as non-hazardous residual material. 100 = No solid waste generated.
ENV-2	Solid outputs (outputs from the system)	Quantity of Solid Output	Measure of the amount of solid output generated by the option. Includes wastes and by-products.	-
ENV-3	Solid outputs (outputs from the system)	Solid Output Re-Use	Measure of the percentage of the solid discharge that will be re-used for other purposes, thus reducing the amount of virgin materials consumed.	-

ENV-4	Gaseous outputs (outputs from the system)	Greenhouse Gas Emissions	Comparison of the estimated quantity of GHG emitted by the various options. Covers anthropogenic emissions of the greenhouse gases measured in the unit of tonnes CO_2-equivalent. Include energy and equipment emissions as well as fugative process emissions (e.g. methane).	-
ENV-5	Gaseous outputs (outputs from the system)	Air Quality	Assesses the impact of gaseous emissions upon air quality in the vicinity of the site. Just some of the emissions of concern are ozone, carbon monoxide, particulate matter (PM10, PM2,5, SPM, black smoke), sulphur dioxide, nitrogen dioxide, nitrogen monoxide, volatile organic compounds including benzene (VOCs) and lead. Use of ozone-depleting substances (ODS) such as CFCs should be prohibited. Local regulations / guidelines should be considered for evaluation of this indicator.	0 = Option meets regulatory requirements only. 33 = "Emission quality surpasses regulatory requirements for < 50% of the required discharge quality parameters. 66 = "Emission quality surpasses regulatory requirements for > 50% of the required discharge quality parameters 100 = Emission quality meets industry best-practice standards and guidelines
ENV-6	Gaseous outputs (outputs from the system)	Green house gas offset	Comparison of the estimated quantity of GHG offset by the various options. The greenhouse gases measured in the unit of tonnes CO_2-equivalent.	-
ENV-7	Liquid outputs-discharge	Quality of Wastewater	Assesses the quality of the discharged liquid waste.	0 = Option meets regulatory requirements only.

	(outputs from the system)	Discharge	A measure of the quality of the liquids being discharged by the option (all output liquids discharged from the system including wastes including byproducts and others). Local regulations / guidelines are applicable for including: BOD, COD, pH, TSS, N, P, heavy metals, toxicity. Any post-treatment steps that may be required in order to meet the regulations are to be accounted for.	33 = Discharge quality surpasses regulatory requirements for < 50% of the required discharge quality parameters. 66 = Discharge quality surpasses regulatory requirements for > 50% of the required discharge quality parameters. 100 = Discharge meets industry best-practice standards and guidelines.
ENV-8	Liquid outputs-discharge (outputs from the system)	Liquid Output Re-Use	Measure of the percentage of the liquid discharge that will be re-used for other purposes, thus reducing the amount of virgin materials consumed. Percentage of liquid output that will be used for useful purposes rather than being disposed of.	-
ENV-9	Liquid outputs-discharge (outputs from the system)	Fuel / Oil Recovered	Measure of the amount of fuel / oil recovered from the process	-
ENV-10	Mass & Energy Inputs to the System	Energy Consumption	Comparison of the net energy consumption of the options, assessing the environmental impact of the option through natural resource depletion. Covers both direct and/or indirect energy consumption including transportation, fuel, electricity,	-

			natural gas, heating oil, etc. The use of renewable energy and co-generation is positively accounted for.	
ENV-11	Impacts of the System	Impacts of Failure on Natural Environment	Evaluates the likely impact on the receiving environment caused through system malfunction of the option. Includes impacts at and adjacent to the site location and emission (liquid, solid and gaseous) discharge points. Classification of indicators to be made on a project by project basis depending on local flora and fauna conditions.	0 = Significant potential impact: High possibilities of failure / No redundancy to prevent discharges "out of specs" to a water body. 25 = Major potential impact: Major possibilities of failure / No redundancy to prevent discharges "out of specs" to municipal treatment plant. 75 = Moderate potential impact: Moderate possibilities of failure with redundancy to prevent discharges "out of specs". 100 = Minor potential impact: Low possibilities of failure with redundancy to prevent discharges "out of specs".
ENV-12	Impacts of the System	Potential Impacts upon Ecological Integrity	Evaluates the potential impacts of the option on ecological integrity: habitat disruption and/or species diversity (health, growth, interactions, density, composition and distribution) with an emphasis on rare, threatened, endangered, native and beneficial animal and plant species. Includes impacts at and adjacent to the site location and emission (liquid, solid and gaseous) discharge points. Classification of indicators to be	0 = Flora and fauna permanently impacted. 50 = Flora and fauna impacted with partial recovery expected in the medium to short term. 75 = Flora and fauna impacted with full recovery expected in the short term. 100 = Minimal disruption, short-term, occasional impacts on flora and fauna.

			made on a project by project basis depending on local flora and faun	

Table C.2 : Dimension Social - List of Selected Indicators.

Code	Theme	Indicator	Description	Scoring Scheme
SOC-1	Health & Safety	Public Health &Safety	Potential adverse impacts on human health and safety arising from the implementation of the option (residents, transients).	0 = Significant potential impact on the community 33 = Moderate potential impact on the community 66 = Low potential impact on the community 100 = No anticipated impact on the community
SOC-2	Health & Safety	Workers Health & Safety	Evaluates the potential impacts of the option for the health and safety of the Corporation and contractor staff (accidents, time off, illness, etc.) Evaluation is to be based upon the track record of the option in similar circumstances.	0 = Includes activities of HIGH risk (This assumes that there is a fatal-flaw analysis - if risk of VERY HIGH / EXTREME found). 33 = All activities LOW or MODERATE risk. 66 = All activities LOW or MODERATE risk. Majority of activities LOW risk 100 = All activities LOW risk
SOC-3	Health & Safety	Hazardous Materials	Assesses the extent of hazardous materials (definition varies by jurisdiction) used (input materials) or generated by the options (emissions). Classification is be made on the UN Globally Harmonized System of Classification and Labelling of Chemical (GHS) using the	0 = Use of materials assigned the signal word "danger" 50 = Use of materials assigned the signal word "warning" 100 = No use of materials with an assigned signal word

			information presented in the MSDS.	
SOC-4	Quality of Life	Disruption of Construction Work on the Community	Assesses the potential disruption and corresponding impact on the community during construction of the option. Disruption includes duration, noise, visual, dust, vibration and community inconvenience.	0 = High impact 20 = Medium impact, re-occurring, long duration (>1 week) 40 = Medium impact, re-occurring, medium duration (1 day - 1 week) 60 = Medium impact, once-off, medium duration (1 day - 1 week) 80 = Medium impact, once-off, short duration (<1 day) 100 = Low Impact
SOC-5	Quality of Life	Disruption of Operations on the Community	Assesses the potential disruption and corresponding impact on the community during operation of the option.	0 = High impact 25 = Medium impact, long duration (average >1 week/month) 50 = Medium impact, medium duration (average 1 day - 1 week/month) 75 = Medium impact, short duration (average <1 day/month) 100 = Low impact
SOC-6	Local Economic Benefits	Economic Advantages for the Local Community	Spin-off benefits to the local community resulting from the implementation of the option.	0 = No local benefits / sourcing from local community 33 = Low: Less than 33% of the procurement from local community 66 = Moderate: Less than 66% of the procurement from local community 100 = High: 66% and more of the

				procurement from local community
SOC-7	Local Economic Benefits	Local Job Creation & Diversity	Assesses the intensity of local job creation and encourages the participation of individuals who identify with minority groups.	0 = Negligible impact on employment opportunities for locals 25 = Significant (>25% or more of the labour component of the total budget) temporary or seasonal employment opportunities for locals. 50 = Significant, temporary or seasonal employment opportunities for locals, including deliberate efforts to hire minority and/or low-income groups. 75 = Significant, permanent employment opportunities for locals. 100 = Significant, permanent employment opportunities for locals, including deliberate efforts to hire minority and/or low-income groups.
SOC-8	Corporate Citizenship	Response to Social Sensitivity	Extent to which the option addresses public sensitivities and concerns. Not applicable if there are no third party / public stakeholders concerned or affected by the project.	0 = Option fails to address public sensitivities and concerns: option likely to be perceived very negatively by the public 33 = Option partially fails to address public sensitivities and concerns: option likely to be perceived somewhat negatively by the public 66 = Option to partially address

				public sensitivities and concerns: option likely to be perceived somewhat positively by the public 100 = Option to address most of the public sensitivities and concerns: option likely to be perceived positively by the public

Table C.3 : Dimension Economic - List of Selected Indicators.

Code	Theme	Indicator	Description	Scoring Scheme
ECO-1	Cost	NPV (Total Project Costs	Measures the present value of the total project costs (including initial capital expenditure, O&M expenses and decommissioning) over the life of the project.	-
ECO-2	Annual tailings handling costs	Biogas recovery	Combustion of recovered methane instead of fossil fuel (oil in this case), saves money.	-
ECO-3	Annual tailings handling costs	Biomass selling	Produced biomass in the anaerobic reactor is sold and brings money to the plant.	-
ECO-4	Minimize Costs	Carbon credit	it refers to the carbon offset and its related revenue for the plant	-
ECO-5	Impact on Economic Activities	Potential for Fines, Penalties and Surcharges	Evaluation of the likelihood of potential action occuring / being avoided through implementation of the option or incurred through malfunction / failures.	0 = High potential for fines, penalties and surcharges. 33 = Medium potential for fines, penalties and surcharges. 66 = Low potential for fines, penalties and surcharges.

				100 = No potential for fines, penalties and surcharges.

C.2.2 Indicator Weighting

The weighting of indicators (and theme if applicable) is presented per dimension, in the tables below.

Table C.4 : Dimension Environmental - Weighting

Theme	**Indicator**	**Indicator Weight**
Solid outputs (outputs from the system)	ENV-1, Quality of Solid Waste	40
Solid outputs (outputs from the system)	ENV-2, Quantity of Solid Output	100
Solid outputs (outputs from the system)	ENV-3, Solid Output Re-Use	100
Gaseous outputs (outputs from the system)	ENV-4, Greenhouse Gas Emissions	100
Gaseous outputs (outputs from the system)	ENV-5, Air Quality	80
Gaseous outputs (outputs from the system)	ENV-6, Green house gas offset	100
Liquid outputs-discharge (outputs from the system)	ENV-7, Quality of Wastewater Discharge	100
Liquid outputs-discharge (outputs from the system)	ENV-8, Liquid Output Re-Use	20
Liquid outputs-discharge (outputs from the system)	ENV-9, Fuel / Oil Recovered	100
Mass & Energy Inputs to the System	ENV-10, Energy Consumption	100
Impacts of the System	ENV-11, Impacts of Failure on Natural Environment	80
Impacts of the System	ENV-12, Potential Impacts upon Ecological Integrity	80

Table C.5 : Dimension Social - Weighting

Theme	Indicator	Indicator Weight
Health & Safety	SOC-1, Public Health & Safety	100
Health & Safety	SOC-2, Workers Health & Safety	100
Health & Safety	SOC-3, Hazardous Materials	20
Quality of Life	SOC-4, Disruption of Construction Work on the Community	60
Quality of Life	SOC-5, Disruption of Operations on the Community	100
Local Economic Benefits	SOC-6, Economic Advantages for the Local Community	100
Local Economic Benefits	SOC-7, Local Job Creation & Diversity	100
Corporate Citizenship	SOC-8, Response to Social Sensitivity	100

Table C.6 : Dimension Economic - Weighting

Theme	Indicator	Indicator Weight
Cost	ECO-1, NPV (Total Project Costs)	100
Annual tailings handling costs	ECO-2, Biogas recovery	100
Annual tailings handling costs	ECO-3, Biomass selling	100
Minimize Costs	ECO-4, Carbon credit	100
Impact on Economic Activities	ECO-5, Potential for Fines, Penalties and Surcharges	80

C.3 Evaluation of Options

C.3.1 Quantitative Evaluation

The numerical values derived for the evaluation of selected quantitative indicators are provided per dimension in the tables below for each option under consideration.

Table C.7 : Dimension Environmental - Quantitative Evaluation of Indicators.

Indicator	Units	Aerobic Treatment	Hybrid treatment	Hybrid treatment+CO_2	Hybrid treatment+CO_2
ENV-2, Quantity of Solid Output	kg/min	22.3	9.66	9.66	9.66
ENV-3, Solid Output Re-Use	%	0	13.8	13.8	13.8
ENV-4, Greenhouse Gas Emissions	tonnes CO_2e	2088725	400800	406500	514500
ENV-8, Liquid Output Re-Use	%	0	0	0	0
ENV-9, Fuel / Oil Recovered	L/min	0	22.45	22.83	31.773
ENV-10, Energy Consumption	GJ PFE	6554774	1676180	1695706	1695706
ENV-6, Green house gas offset	tonnes CO_2e	0	5885735	6183243	8849821

Table C.8 : Dimension Economic - Quantitative Evaluation of Indicators.

Indicator	Units	Aerobic Treatment	Hybrid treatment	Hybrid treatment+CO_2	Hybrid treatment+CO_2
ECO-1, NPV (Total Project Costs)	$	261375100	102005900	114737300	114737300
ECO-4, Carbon credit	$	0	38257290	40191080	57523830
ECO-2, Biogas recovery	$	0	194190000	198000000	274860000
ECO-3, Biomass selling	$	0	8280000	8280000	8280000

Whenever applicable, details are provided to justify the scoring of each option with respect to the selected indicators. The details are presented in the tables below.

Table C.9 : Dimension Environmental - Quantitative Evaluation of Indicators : Comments.

Indicator	Aerobic Treatment	Hybrid treatment	Hybrid treatment+CO_2	Hybrid treatment+CO_2
ENV-2, Quantity of Solid Output	22.298 kg/min solid output from aerobic bioreactor	8.33kg/min solid output from anaerobic treatment and 0.005m3/min solid output(=1.3 kg dry/min) from aerobic reactor. Total=9.66 kg/min solid output	8.33kg/min solid output from anaerobic treatment and 0.005m3/min solid output(=1.3 kg dry/min) from aerobic reactor. Total=9.66 kg/min solid output.	8.33kg/min solid output from anaerobic treatment and 0.005m3/min solid output (=1.3 kg dry/min) from aerobic reactor. Total=9.66 kg/min solid output.
ENV-3 Solid Output Re-Use	Solid waste is land filled.	Solid waste from aerobic reactor is landfilled and solid waste from anaerobic reactor is sold for more use. Solid output from anaerobic reactor is 14% of total solid output from anaerobic and aerobic reactor.	Solid waste from aerobic reactor is landfilled and solid waste from anaerobic reactor is sold for more use. Solid output from anaerobic reactor is 14% of total solid output from anaerobic and aerobic reactor.	Solid waste from aerobic reactor is landfilled and solid waste from anaerobic reactor is sold for more use. Solid output from anaerobic reactor is 14% of total solid output from anaerobic and aerobic reactor.
ENV-9, Fuel / Oil Recovered	no methane recovery.	The recovered methane is equal to 22.45 l /min oil saving	The recovered methane is equal to 22.83 to 31.773 l/min oil saving.	The recovered methane is equal to 22.83 to 31.773 l/min oil saving.
ENV-10 Energy Consumption	Energy consumption for aerobic treatment equals to 60692346kWh/y (218492.4456 GJ/y). This equals	The overall required energy for anaerobic treatment is 347097 kWh/y.Power requirement for aerobic treatment is assumed to be	The overall required energy for scrubber=180795.5 kWh/y. For anaerobic treatment is 347097 kWh/y. Power requirement for aerobic	The overall required energy for scrubber=180795.5 kWh/y and for anaerobic treatment is 347097 kWh/y. Power requirement for aerobic

	to 6554773 GJ in 30 years	15173086.5kWh/y.Therefore the total energy for hybrid treatment =15520183.5 kWh/y (55873 GJ/y). It equals to 1676179.8 Gj in 30 years	treatment is assumed to be 15173086.5kWh/y. Therefore the total energy for the developed hybrid treatment process in the present work=15700979 kWh/y (56523.5244 GJ/y). This equals to 1695705.732 GJ in 30 years.	treatment is assumed to be 15173086.5kWh/y. Therefore the total energy consumption in a developed hybrid treatment process in the present work=15700979 kWh/y (56523.5244 GJ/y). This equals to 1695706 Gj in 30 years
ENV-4 Greenhouse Gas Emissions	11359.5 tonnes CO_2e/y (GHG) from sludge landfilling and 58264.6 tonnes CO_2/y (GHG) from power generation=69624 tonnes CO2e/y (GHG). In 30 years it equals to 2088725.1 tonnes CO_2e	The GHG emissions in 30 years equal to 400800 tonnes CO_2e	The GHG emissions in 30 years equal to 406500 tonnes CO_2e	The GHG emissions in 30 years equal to 514500 tonnes CO_2
ENV-8, Liquid Output Re-Use	No liquid reuse.	No liquid reuse.	No liquid reuse.	No liquid reuse.

Table C.10 : Dimension Economic - Quantitative Evaluation of Indicators : Comments.

Indicator	Aerobic Treatment	Hybrid treatment	Hybrid treatment+CO_2	Hybrid treatment+CO_2
ECO-1 NPV (Total Project Costs)	The cost of power generation and sludge landfilling= 8383503 $/y so in 30 years=251505090 $, capital cost of aerobic treatment for 50 years duration of project=16.45M$(=9.87M$ in 30 years project duration). Therefore the total cost in 30 years 261375100$	The operating cost of aerobic treatment is approximately 2194476 $/y which equals to 65834280$ in 30 years. The capital cost of aerobic treatment for 30 years project duration=9.87, so total cost of aerobic treatment in 30 years=75704280$.In anaerobic treatment the cost of power generation=43387$/y, and capital cost=25M$ for 30 yeras project, so in 30 years total cost=26301610.Therefore the total aerobic and anaerobic costs in 30 years=102005890$	Aerobic treatment operation costs 2194476 $/y=65834280$ in 30 years. The capital cost of aerobic treatment=9.87M$ for 30 years, so total cost of aerobic treatment in 30 years=75704280$.In anaerobic treatment, power generation costs 43387$/y(=1301610$ in 30 years),Annualized cost of applying scrubber=424381$/y(= 12731430$ in 30 years) capital cost of anaerobic treatment=25M$, so total cost of anaerobic treatment in 30 years=39033040 and the total cost of hybrid treatment in 30 years=114737320 $	Aerobic treatment operation costs 2194476 $/y=65834280$ in 30 years. The capital cost of aerobic treatment=9.87M$ for 30 years, so total cost of aerobic treatment in 30 years=75704280$.In anaerobic treatment, power generation costs 43387$/y(=1301610$ in 30 years),Annualized cost of applying scrubber=424381$/y(=12 731430$ in 30 years) capital cost of anaerobic treatment=25M$, so total cost of anaerobic treatment in 30 years=39033040 and the total cost of hybrid treatment in 30 years=114737320 $
ECO-4 Carbon credit	No carbon offset and therefore no carbon credit.	Carbon credit=0.15M $/y saving(=4.5M$ in 30 years)	Carbon credit=0.19 to 0.32 M$/y saving (=5.7 to 9.6 M$ in 30 years).	Carbon credit=0.19 to 0.32 M$/y saving (=5.7 to 9.6 M$ in 30 years).
ECO-3	All produced	Selling the biomass	Selling the biomass	Selling the biomass from

Biomass selling	biomass were landfilled	from anaerobic reactor gives 276000$/y cash entry=8280000$ in 30 years	from anaerobic reactor gives 276000$/y cash entry=8280000$ in 30 years	anaerobic reactor gives 276000$/y cash entry=8280000$ in 30 years

C.3.2 Qualitative Evaluation

The evaluation of options is presented per dimension in the tables below. Scores have been assigned for each applicable indicator.

Table C.11 : Dimension Environmental - Evaluation of Indicators.

Indicator	**Aerobic Treatment**	**Hybrid treatment**	**Hybrid treatment+CO_2**	**Hybrid treatment+CO_2**
ENV-1, Quality of Solid Waste	0	0	0	0
ENV-2, Quantity of Solid Output	0	57	57	57
ENV-3, Solid Output Re-Use	0	14	14	14
ENV-4, Greenhouse Gas Emissions	0	59	59	54
ENV-5, Air Quality	0	33	66	66
ENV-6, Green house gas offset	0	67	70	100
ENV-7, Quality of Wastewater Discharge	100	100	100	100
ENV-8, Liquid Output Re-Use	0	0	0	0
ENV-9, Fuel / Oil Recovered	0	71	72	100
ENV-10, Energy Consumption	0	74	74	74
ENV-11, Impacts of Failure on Natural Environment	75	75	75	75
ENV-12, Potential Impacts upon Ecological Integrity	100	100	100	100

Table C.12 : Dimension Social - Evaluation of Indicators.

Indicator	Aerobic Treatment	Hybrid treatment	Hybrid treatment+CO_2	Hybrid treatment+CO_2
SOC-1, Public Health & Safety	100	100	100	100
SOC-2, Workers Health & Safety	66	66	66	66
SOC-3, Hazardous Materials	100	100	100	100
SOC-4, Disruption of Construction Work on the Community	60	60	60	60
SOC-5, Disruption of Operations on the Community	100	100	100	100
SOC-6, Economic Advantages for the Local Community	100	100	100	100
SOC-7, Local Job Creation & Diversity	75	75	75	75
SOC-8, Response to Social Sensitivity	33	66	100	100

Table C.13 : Dimension Economic - Evaluation of Indicators.

Indicator	Aerobic Treatment	Hybrid treatment	Hybrid treatment+CO_2	Hybrid treatment+CO_2
ECO-1, NPV (Total Project Costs)	0	61	56	56
ECO-2, Biogas recovery	0	71	72	100
ECO-3, Biomass selling	0	10	10	10
ECO-4, Carbon credit	0	67	70	100
ECO-5, Potential for Fines, Penalties and Surcharges	66	100	100	100

Whenever applicable, details are provided to justify the evaluation of each option with respect to the selected indicators. The details are presented in the tables below.

Table C.14: Dimension Environmental - Evaluation of Indicators : Comments.

Indicator	**Aerobic Treatment**	**Hybrid treatment**	**Hybrid treatment+CO_2**	**Hybrid treatment+CO_2**
ENV-1 Quality of Solid Waste	Solid waste is from activated sludge process and is a biological floc composed of bacteria and protozoa, therefore is a hazardous waste.	Solid waste is from activated sludge process and is a biological floc composed of bacteria and protozoa, therefore is a hazardous waste.	Solid waste is from activated sludge process and is a biological floc composed of bacteria and protozoa, therefore is a hazardous waste.	Solid waste is from activated sludge process and is a biological floc composed of bacteria and protozoa, therefore is a hazardous waste.
ENV-5 Air Quality	Option meets regulatory requirements only.	Emission quality surpasses regulatory requirements for < 50% of the required discharge quality parameters.	Emission quality surpasses regulatory requirements for > 50% of the required discharge quality parameters	Emission quality surpasses regulatory requirements for > 50% of the required discharge quality parameters
ENV-7, Quality of Wastewater Discharge	Discharge meets industry best-practice standards and guidelines.	Discharge meets industry best-practice standards and guidelines.	Discharge meets industry best-practice standards and guidelines.	Discharge meets industry best-practice standards and guidelines.
ENV-11, Impacts of Failure on Natural Environment	Moderate potential impact: Moderate possibilities of failure with redundancy to prevent discharges “out of specs”.	Moderate potential impact: Moderate possibilities of failure with redundancy to prevent discharges “out of specs”.	Moderate potential impact: Moderate possibilities of failure with redundancy to prevent discharges “out of specs”.	Moderate potential impact: Moderate possibilities of failure with redundancy to prevent discharges “out of specs”.
ENV-12, Potential Impacts upon Ecological Integrity	Minimal disruption, short-term, occasional impacts on flora and fauna.	Minimal disruption, short-term, occasional impacts on flora and fauna.	Minimal disruption, short-term, occasional impacts on flora and fauna.	Minimal disruption, short-term, occasional impacts on flora and fauna.

Table C.15: Dimension Social - Evaluation of Indicators : Comments.

Indicator	Aerobic Treatment	Hybrid treatment	Hybrid treatment+CO_2	Hybrid treatment+CO_2
SOC-1, Public Health & Safety	No anticipated impact on the community	No anticipated impact on the community	No anticipated impact on the community	No anticipated impact on the community
SOC-2, Workers Health & Safety	All activities LOW or MODERATE risk. Majority of activities LOW risk. Ex: methane generated from landfill can cause fire.	All activities LOW or MODERATE risk. Majority of activities LOW risk. Ex: methane generated from landfill can cause fire.	All activities LOW or MODERATE risk. Majority of activities LOW risk. Ex: methane generated from landfill can cause fire.	All activities LOW or MODERATE risk. Majority of activities LOW risk. Ex: methane generated from landfill can cause fire.
SOC-3, Hazardous Materials	No use of materials with an assigned words "Danger" and "Warning"	No use of materials with an assigned words "Danger" and "Warning"	No use of materials with an assigned words "Danger" and "Warning"	No use of materials with an assigned words "Danger" and "Warning"
SOC-4 Disruption of Construction Work on the Community	Disruption of construction work has once-off, medium impact on the Community with duration about 1 day to 1 week.	Disruption of construction work has once-off, medium impact on the Community with duration about 1 day to 1 week.	Disruption of construction work has once-off, medium impact on the Community with duration about 1 day to 1 week.	Disruption of construction work has once-off, medium impact on the Community with duration about 1 day to 1 week.
SOC-5, Disruption of Operations on the Community	Low impact	Low impact	Low impact	Low impact
SOC-6, Economic Advantages for the Local	High: 66% and more of the procurement from local community	High: 66% and more of the procurement from local community	High: 66% and more of the procurement from local community	High: 66% and more of the procurement from local community

Community				
SOC-7 Local Job Creation & Diversity	Significant, permanent employment opportunities for locals.	Significant, permanent employment opportunities for locals.	Significant, permanent employment opportunities for locals.	Significant, permanent employment opportunities for locals.
SOC-8 Response to Social Sensitivity	Option partially fails to address public sensitivities and concerns: Option likely to be perceived somewhat negatively by the public. This method generates lots of solid outputs that are land-filled. This method generates a significant amount of GHG emissions. Also there is no biogas generation.	Option to partially address public sensitivities and concerns: option likely to be perceived somewhat positively by the public. Solid output that is sent to landfill is less than aerobic treatment alone. However this method still sent a lot of solid output to the landfill.In this method biogas is produced which reduces the consumption of fossil fuel and generation of GHG emissions.	Option to address most of the public sensitivities and concerns: Option likely to be perceived positively by the public. Although in this method some solid outputs are landfilled, however it removes most of CO2 emission from industry, produces biogas, and reduces GHG emission significantly.	Option to address most of the public sensitivities and concerns: Option likely to be perceived positively by the public. Although in this method some solid outputs are landfilled, however it removes most of CO2 emission from industry, produces biogas, and reduces GHG emission significantly.

Table C.16: Dimension Economic - Evaluation of Indicators : Comments.

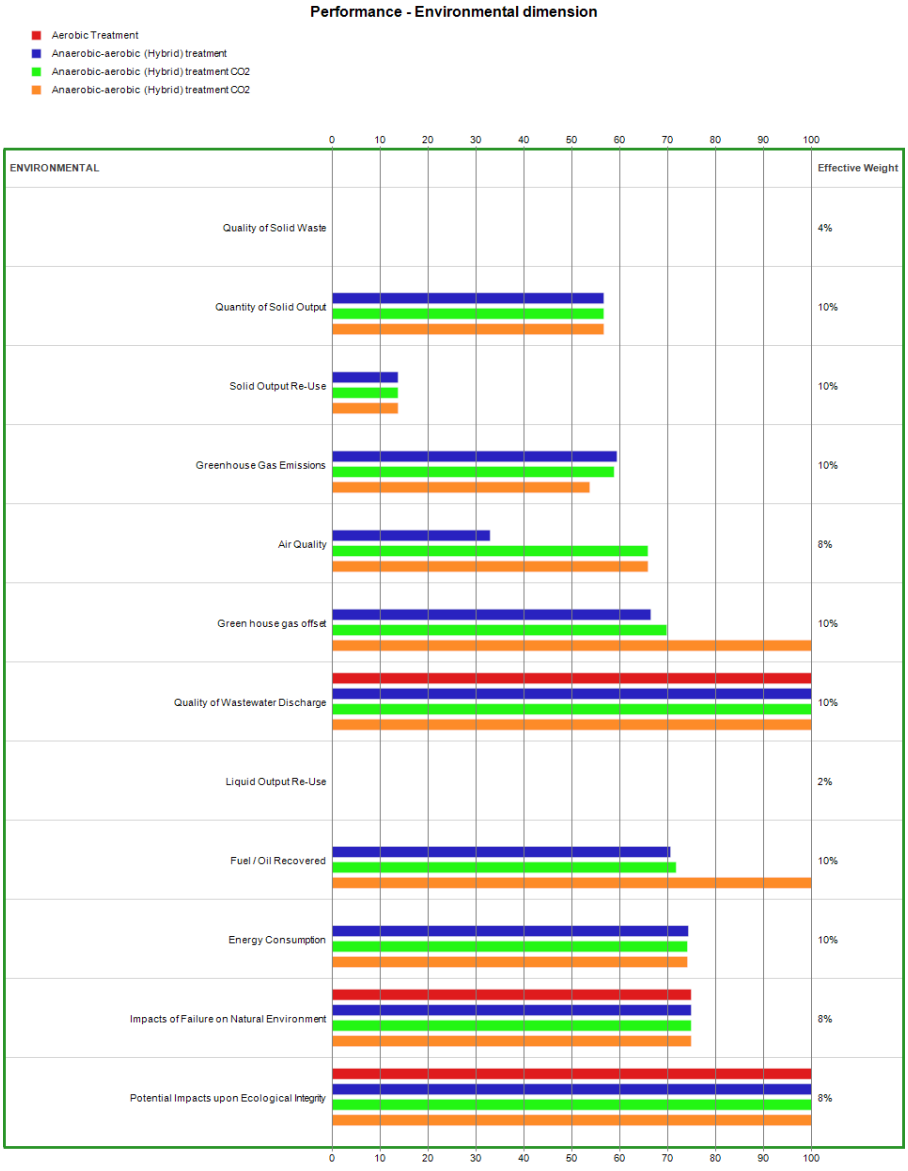
Indicator	Aerobic Treatment	Hybrid treatment	Hybrid treatment+CO_2	Hybrid treatment+CO_2
ECO-5 Potential for Fines, Penalties and Surcharges	Low potential for fines, penalties and surcharges. GHG emissions from aerobic treatment has the potential for fines.	No potential for fines, penalties and surcharges. This method recovers methane that is generated in anaerobic reactor and reduces the GHG emission.	No potential for fines, penalties and surcharges. This method recovers methane that is generated in anaerobic reactor and reduces the GHG emission.	No potential for fines, penalties and surcharges. This method recovers methane that is generated in anaerobic reactor and reduces the GHG emission.

C.4 Detailed Results

In the GoldSET software two types of analysis to be displayed are: Performance (Scores out of 100%) and Strengths and Weaknesses. The types of output to be displayed are histogram and radar.

C.4.1 Indicator-performance-histogram

The results obtained from this evaluation are presented in the figure below.


Performance - Environmental dimension
Aerobic Treatment
Anaerobic-aerobic (Hybrid) treatment
Anaerobic-aerobic (Hybrid) treatment CO2
Anaerobic-aerobic (Hybrid) treatment CO2
0 10 20 30 40 50 60 70 80 90 100
ENVIRONMENTAL
Effective Weight
Quality of Solid Waste
4%
Quantity of Solid Output
10%
Solid Output Re-Use
10%
Greenhouse Gas Emissions
10%
Air Quality
8%
Green house gas offset
10%
Quality of Wastewater Discharge
10%
Liquid Output Re-Use
2%
Fuel / Oil Recovered
10%
Energy Consumption
10%
Impacts of Failure on Natural Environment
8%
Potential Impacts upon Ecological Integrity
8%
0 10 20 30 40 50 60 70 80 90 100

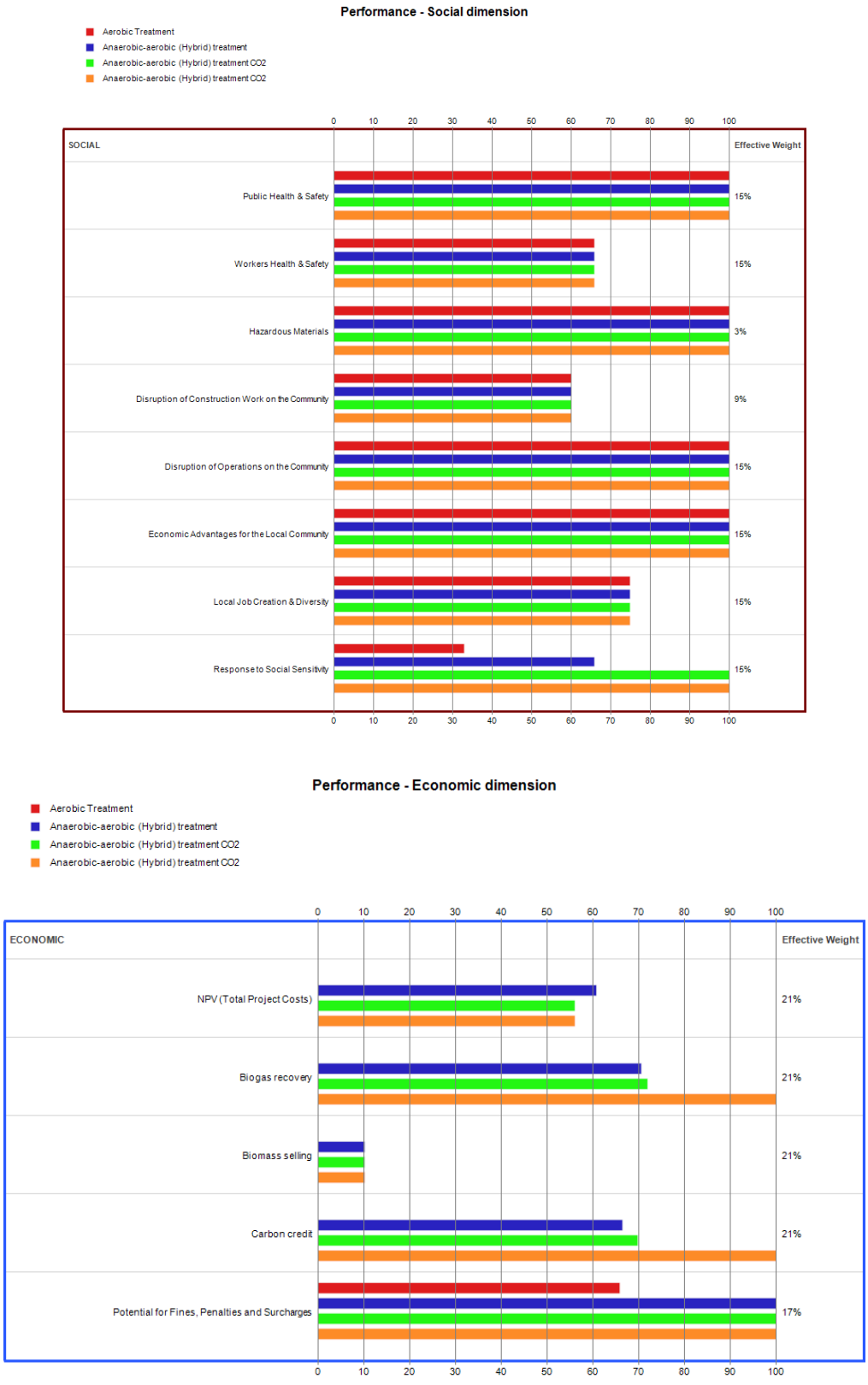
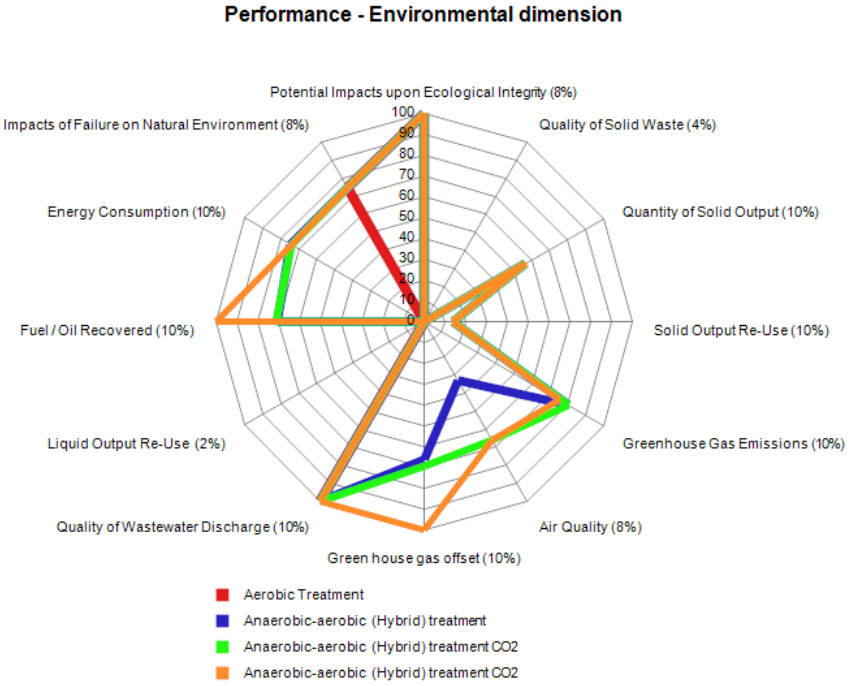
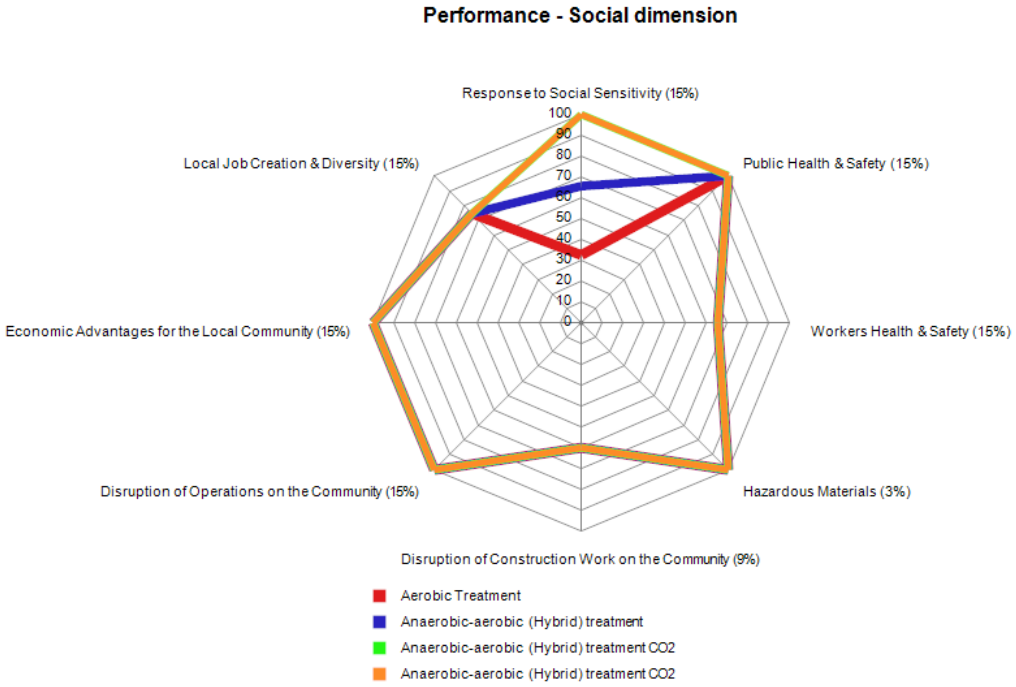


Figure C.1: indicator-performance-histogram

C.4.2 Indicator-performance-radar

The results obtained from this evaluation are presented in the figure below.





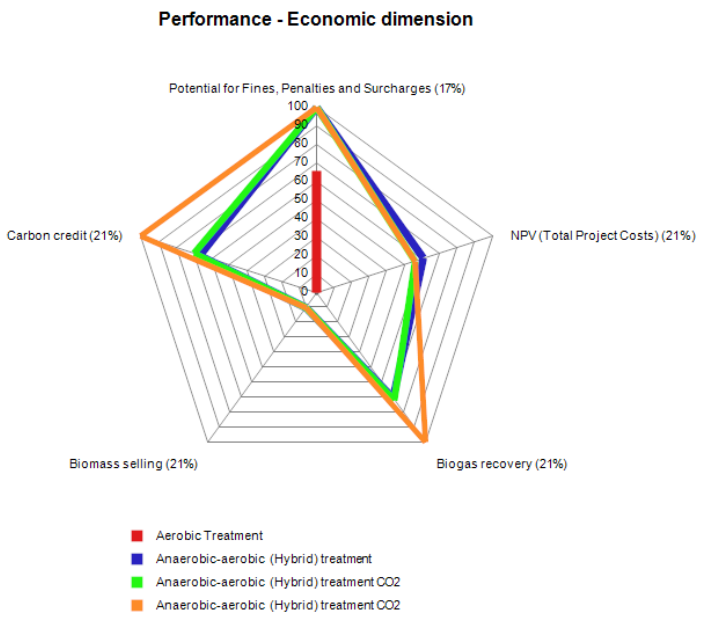
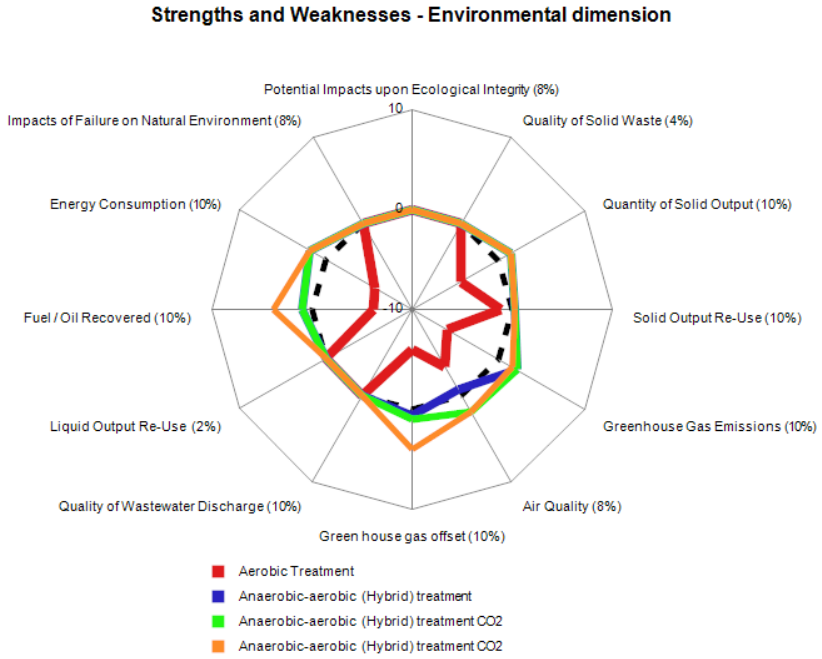
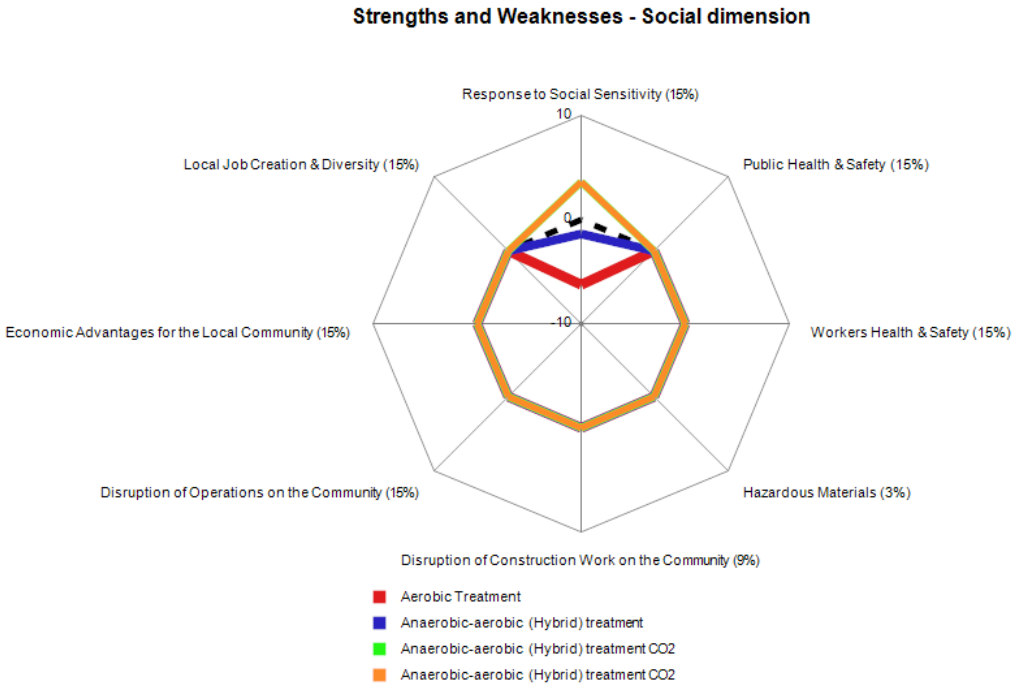


Figure C.2: indicator-performance-radar

C.4.3 Indicator-strength-radar

The results obtained from this evaluation are presented in the figure below.





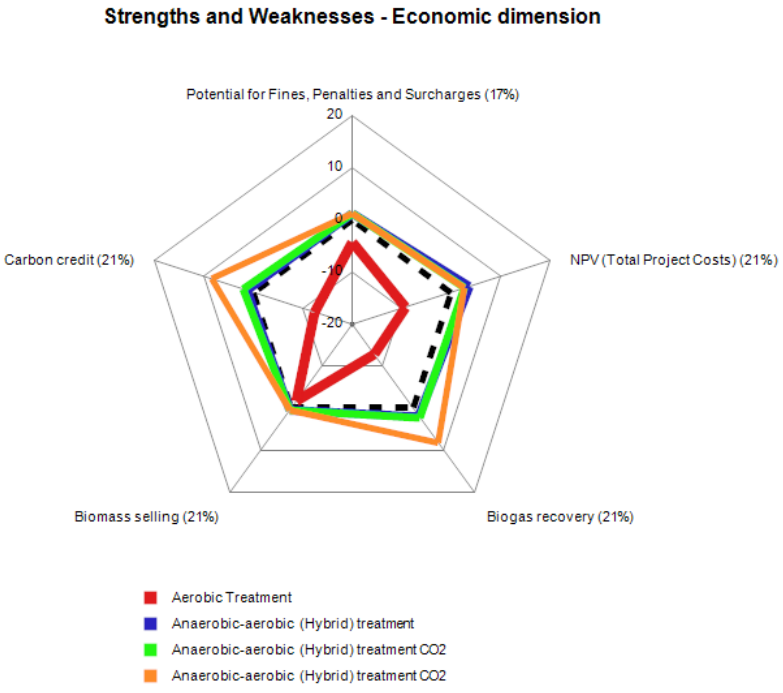
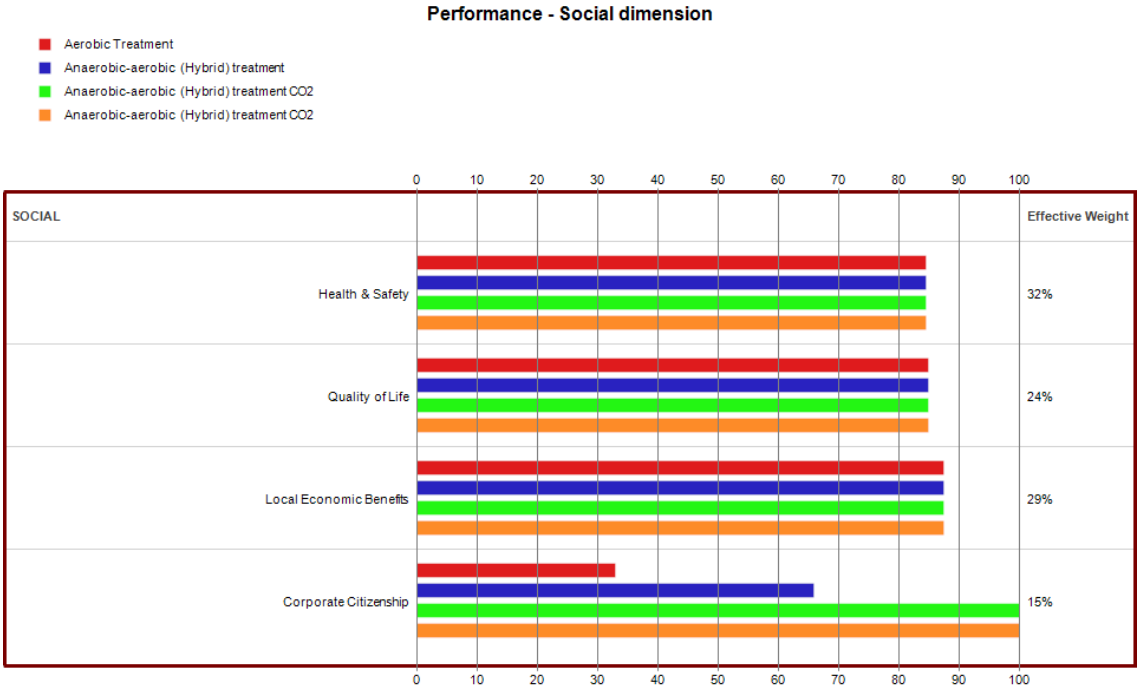


Figure C.3: indicator-strength-radar

C.4.4 Theme-performance-histogram

The results obtained from this evaluation are presented in the figure below.



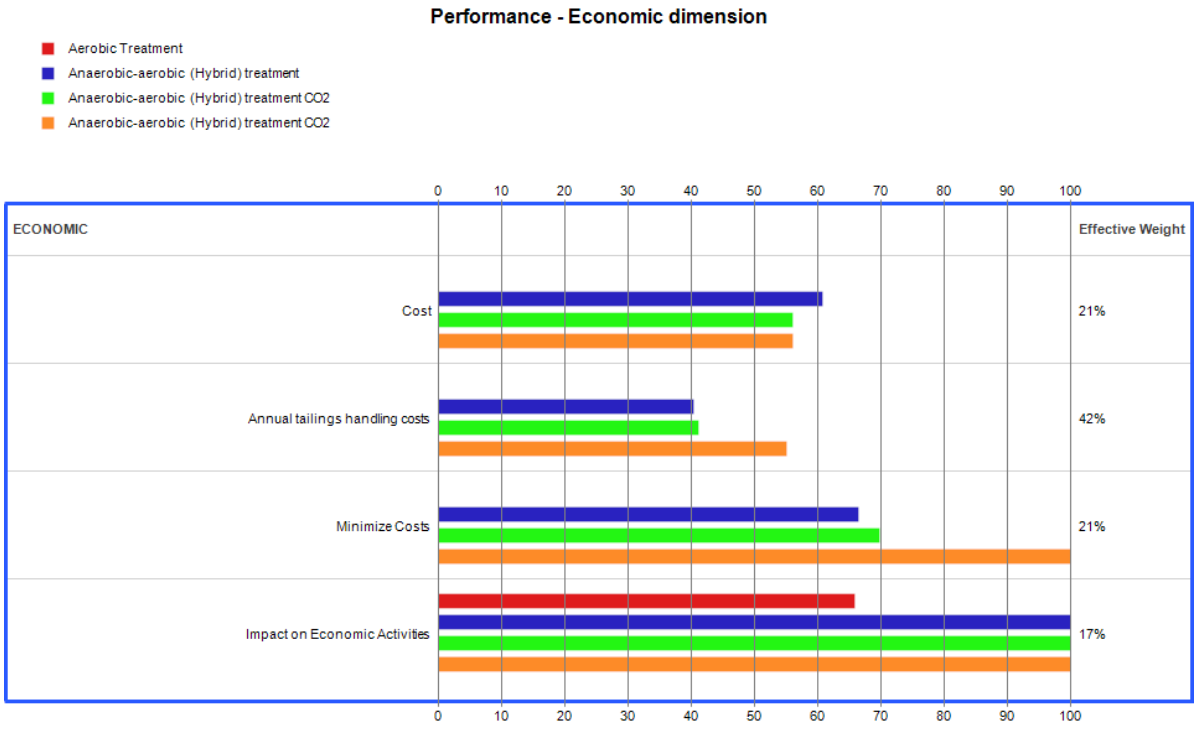
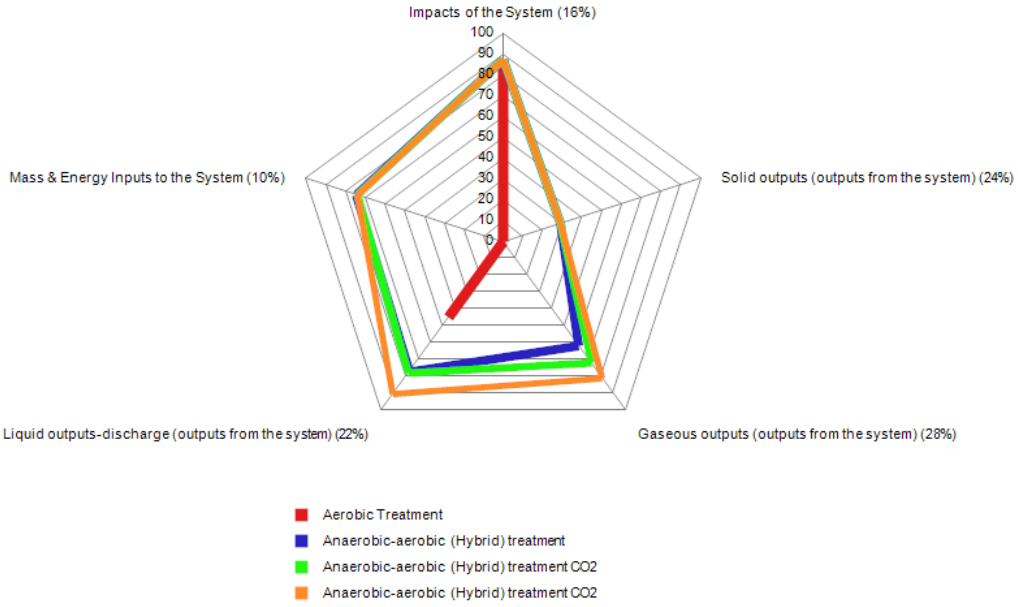


Figure C.4: theme-performance-histogram

C.4.5 Theme-performance-radar

The results obtained from this evaluation are presented in the figure below.

Performance - Environmental dimension



Performance - Social dimension

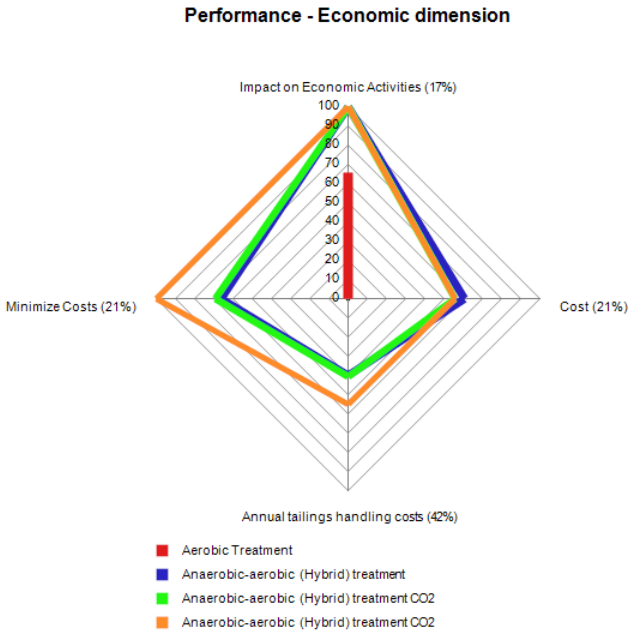
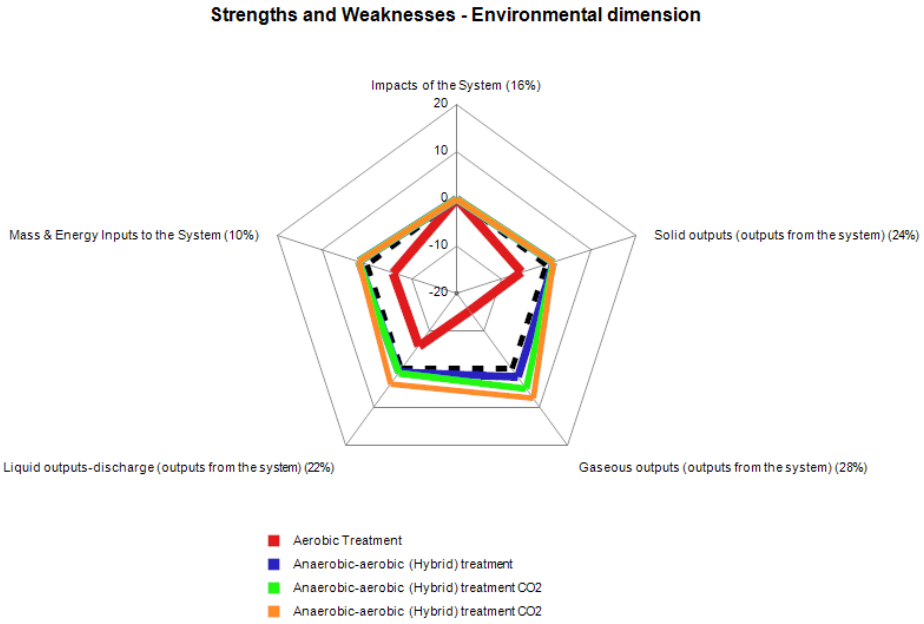
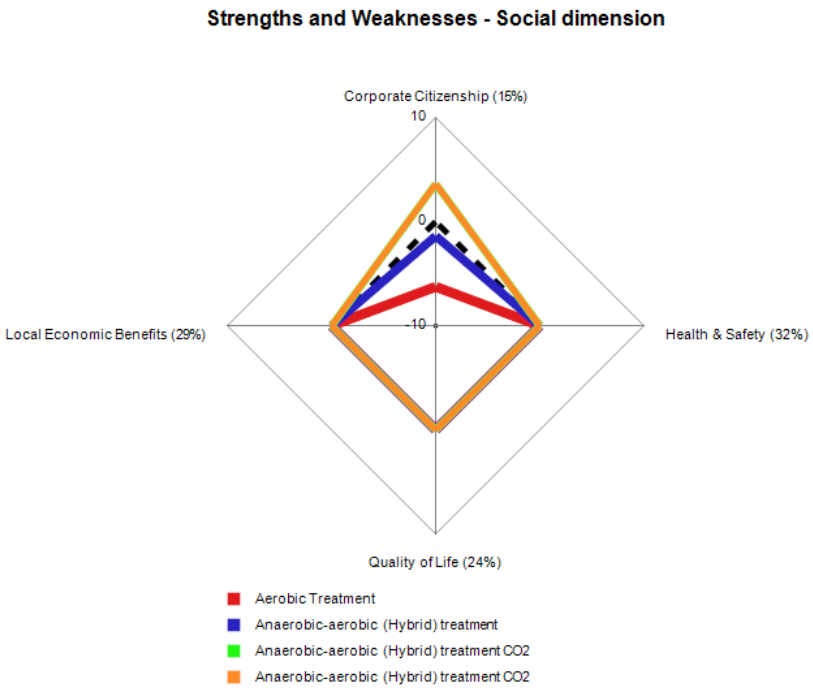


Figure C.5: theme-performance-radar:

C.4.6 Theme-strength-radar

The results obtained from this evaluation are presented in the figure below.





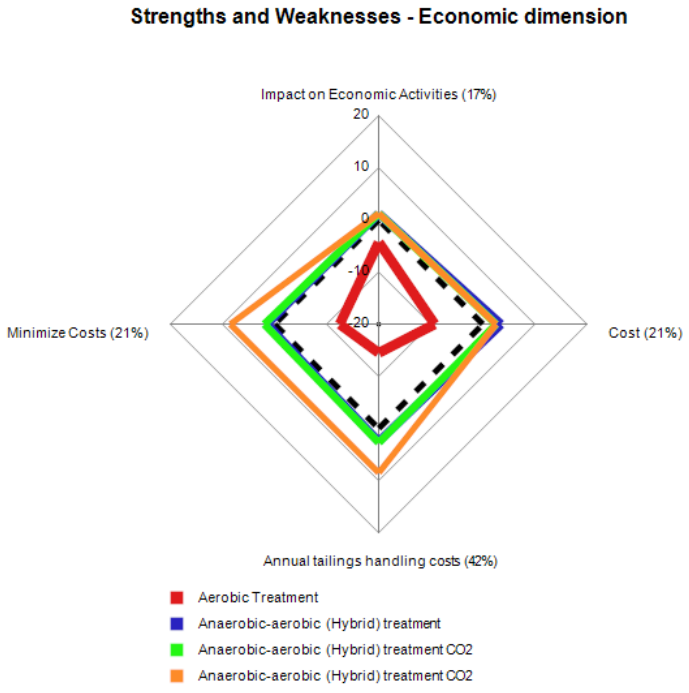
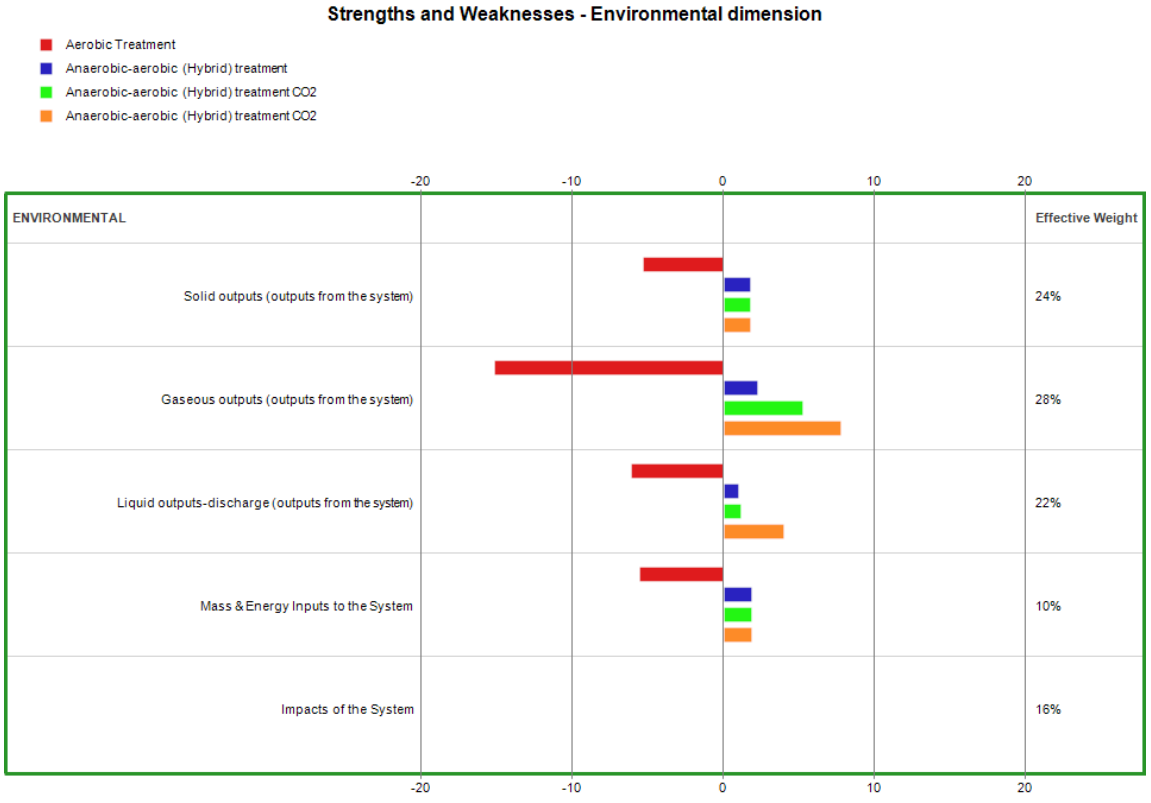
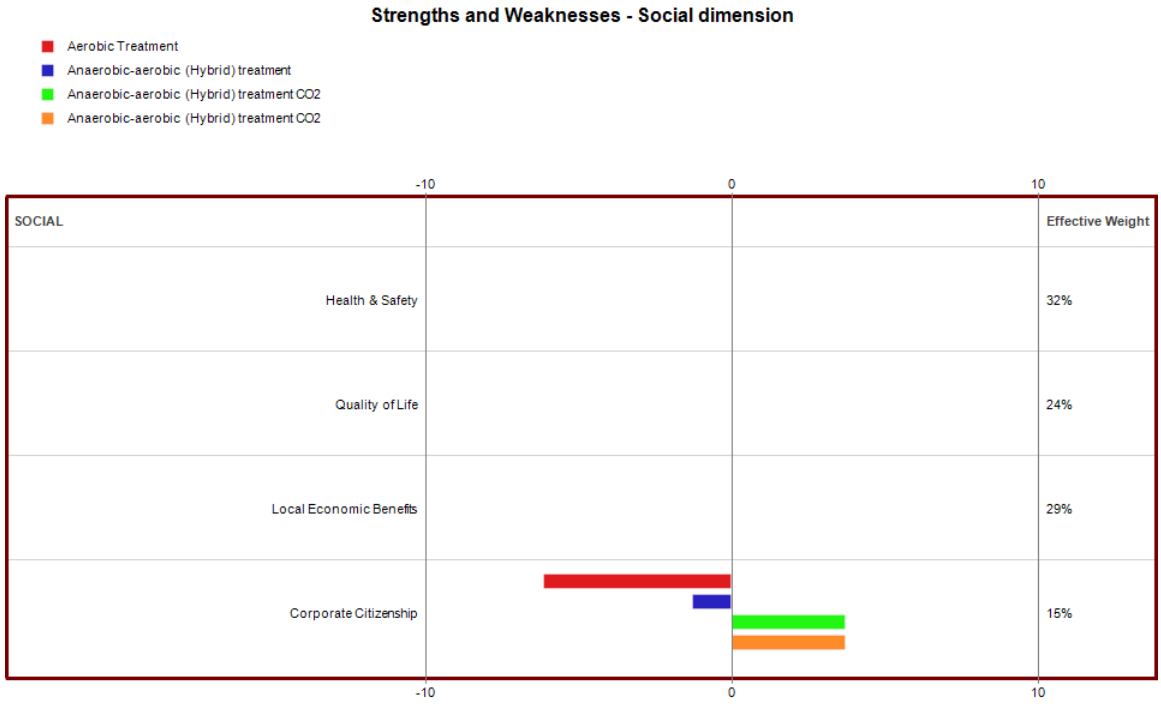


Figure C.6: theme-strength-radar

C.4.7 Theme-strength-histogram

The results obtained from this evaluation are presented in the figure below.





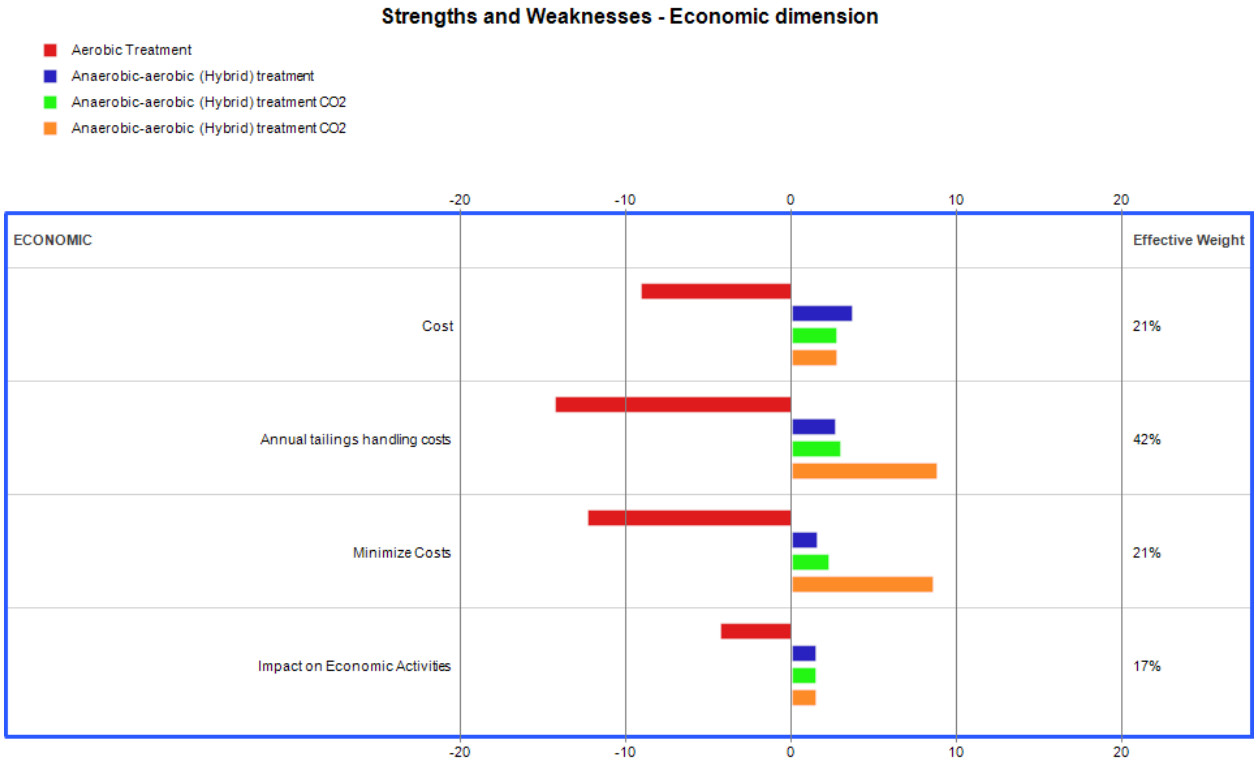


Figure C.7: theme-strength-histogram